A Novel Trinuclear Cobalt Complex: Crystal and Electronic Structure of (Per)4[Co(mnt)2]3

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Single crystals of (Per)4[Co(mnt)2]3 (Per = perylene; mnt = maleonitriledithiolate) were obtained as a minor product of the electrochemical oxidation of perylene and [(n-C4H9)4N][Co(mnt)2]. The structure, solved by X-ray diffraction at room temperature, was monoclinic, space group $P2_1/n$ with cell parameters $a = 12.093(1)$ Å, $b = 20.912(1)$ Å, $c = 16.633(1)$ Å, $\beta = 94.290(6)°$, $V = 4194.5(5)$ Å^3, and $Z = 2$. The crystal structure consists of [Co(mnt)2]3 units and trimers of perylene units with an extra perylene molecule placed perpendicular to this trimer. The EPR spectrum at room temperature shows a narrow (0.4 G) and almost isotropic line at $g = 2.0031$ ascribed to (Per)3[+]. Extended Hückel molecular orbital calculations on this structure support a description of this solid as [Co(mnt)2]3[−](Per)3[+](Per)[0].

Introduction

As part of an effort to prepare new molecular conductors with stacks of paramagnetic counterions, we have recently reported two new conducting compounds based on perylene (Per) and on Co(mnt)2, (where mnt = maleonitriledithiolate or *cis*-2,3-dimercapto-2-butenedinitrile) with two different stoichiometries: (Per)2Co(mnt)2[1] and (Per)Co(mnt)2(CH2Cl2)0.5.[2] Although the crystal structure for the first one has not yet been solved, its lattice parameters and physical properties strongly suggest a structure with dimeric [Co(mnt)2]2 units having the cobalt atoms in a square pyramidal coordination as found in other Co–bis(dithiolate) complexes such as [(n-C4H9)4N][Co(C6-Cl4S2)2][3] or Co[S2C2(CF3)2]2.[4] The perylene-containing compound with a 1:1 stoichiometry was shown to have an unusual polymeric arrangement of Co(mnt)2 units forming a zigzag chain of Co–S bonds with alternating distances of 2.62 and 2.44 Å.

In this paper we report the structure, EPR spectrum, and molecular orbital calculations for a compound with a third stoichiometry, (Per)4[Co(mnt)2]3, obtained as a byproduct during the preparations of the previously reported compounds by electrochemical oxidation. For the first time, the trimeric species [Co(mnt)2]3 is observed.

Experimental Section

Sample Preparation. (Per)4[Co(mnt)2]3 single crystals were obtained in relatively small amounts (≈3–5%) by the electrochemical oxidation of perylene in a dichloromethane solution containing [(n-C4H9)4N][Co(mnt)2] as previously described.[1,2] Typically, an almost saturated solution of perylene (≈10⁻² M) and [(n-C4H9)4N][Co(mnt)2] (≈5 × 10⁻³ M) in dichloromethane was deaerated and placed under argon in the anode compartment of an electrochemical cell with platinum electrodes. After ≈5 days of oxidation performed with constant current (≈2–5 μA for 1 cm² of electrode surface), the crystals formed in the anode compartment

were filtered off and washed with dichloromethane. Small dark crystals of (Per)4[Co(mnt)2]3, typically 0.1 × 0.1 × 0.2 mm³, were found among the other stoichiometries, hardly distinguishable from those of (Per)-Co(mnt)2(CH2Cl2)0.5. A closer observation showed that (Per)4[Co-(mnt)2]3 crystals had usually smaller dimensions and a slightly greenish dark shine. Distinction from (Per)2Co(mnt)2 was relatively easy since the crystals of the latter compound had a distinct thin needle shape.

X-ray Crystallography. An almost black crystal with a dark green shine having approximate dimensions of 0.07 × 0.15 × 0.18 mm³ was glued on top of a glass fiber and transferred to the goniometer mounted on an Enraf-Nonius CAD-4F diffractometer, using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The exact cell dimensions were obtained by a least-squares fit of the orientation matrix to the setting angles of 22 centered high-order reflections from various parts of reciprocal space. The unit cell was identified as monoclinic, space group $P2_1/n$. This choice was confirmed by the solution and the successful refinement of the structure. Reduced cell calculations did not indicate any higher metrical lattice symmetry,[5] and examination of the final atomic coordinates of the structure did not yield extra symmetry elements.[6] The data set was collected at room temperature in a ω–2θ scan mode [Δω = (0.80 + 0.35 tan θ)°]. Crystal and/or instrumental instability was monitored by measurement of the intensities of three reference reflections that were collected after every 2 h of X-ray exposure time; these reflections showed no decomposition during the 179.6 h of X-ray exposure time. The intensity data were corrected for the decay, for the Lorentz and polarization effects, but not for absorption. Standard deviations on the intensities based on counting statistics were increased according to an analysis of the excess variance[7] of the three reference reflections: $\sigma^2(I) = \sigma_{cs}^2(I) + (0.013I)^2$. Equivalent reflections were averaged ($\Sigma\sigma/\Sigma I = 0.058$), resulting in 5825 unique reflections and 3770 reflections satisfying the $I > 2.5\sigma(I)$ criterion of observability.

The structure was solved by Patterson methods and subsequent partial structure expansion (SHELXS86)[8] and difference Fourier maps. The positional and anisotropic thermal displacement parameters for the non-hydrogen atoms were refined with block-diagonal least-squares procedures (CRYLSQ)[9] minimizing the function $Q = \Sigma[w(|F_o|-|F_c|)^2]$. The hydrogen atoms were included in the final refinement riding on their carrier atoms

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Table I. Summary of Crystal Data and Structure Determination Parameters

chem formula	$C_{104}H_{48}Co_3S_{12}N_{12}$
fw	2027.12
space group, No.[15]	$P2_1/n$, 14
a (Å)	12.093(1)
b (Å)	20.912(1)
c (Å)	16.633(1)
β (deg)	94.290(6)
V (Å^3)	4194.5(5)
Z	2
d(calcd) (g/cm^3)	1.605
$F(000)$ (electrons)	2058
μ(Mo Kα) (cm^{-1})	9.3
radiation, λ (Å)	Mo Kα, 0.710 73
temp, (K)	295
θ range; min–max (deg)	0.98–23.0
no. of tot. data	11 675
no. of unique data	5825
no. of obsd data ($I \geq 2.5\sigma(I)$)	3770
R_F, R_{wF}^{a}	0.047, 0.049

^{a} $R_F = \sum(\||F_o| - |F_c|\|)/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum|F_o|^2]^{1/2}$.

with their positions calculated by using sp^2 hybridization at the C atom as appropriate with a fixed C–H distance of 0.98 Å. Final refinement on F_o by full-matrix least-squares techniques with anisotropic thermal displacement parameters for the non-hydrogen atoms and one overall temperature factor for the hydrogen atoms converged at $R_F = 0.047$ ($R_w = 0.049$, $w = 1$, $S = 2.901$). A final difference Fourier synthesis revealed residual densities between –0.41 and 0.56 e/Å^3. Crystal data and experimental details of the structure determination are compiled in Table I, final fractional atomic coordinates and equivalent isotropic thermal displacement parameters for the non-hydrogen atoms are given in Table II, and selected bond distances and bond angles are collected in Table III. Tables of thermal displacement parameters and comprehensive lists of bond angles are given as supplementary material. Scattering factors were those given by Cromer and Mann,[10] and anomalous dispersion factors taken from Cromer and Liberman[11] were included in F_c. All calculations were carried out on the CDC-Cyber 962-31 computer of the University of Groningen with the program packages XTAL[12] and PLATON[13] (calculation of geometric data) and an extended version of the program PLUTO[14] (preparation of illustrations).

EPR. Electron paramagnetic resonance spectra were obtained at room temperature with a conventional X-band spectrometer (Bruker ESP 300). Five crystals, previously identified by X-ray diffraction, were fixed to a signal-free Teflon holder with a minimum amount of Apiezon grease, which was placed inside a quartz tube, which in turn was placed inside the cavity. g factors were determined by simultaneously measuring the microwave frequency (HP-5350B frequency counter) and the magnetic field (ER035M NMR gaussmeter, Bruker).

Molecular Orbital Calculations. All calculations were of the extended Hückel type[16] with modified H_{ij}'s.[17] The basis set for the metal atom consisted of ns, np, and $(n - 1)d$ orbitals. The s and p orbitals were described by single Slater-type wave functions, and the d orbitals were taken as contracted linear combinations of two Slater-type wave functions.

The perylene molecule was considered planar, with C–C and C–H bond lengths, respectively, of 1.40 and 1.08 Å. The square planar Co-(mnt)$_2$ unit was modeled according to the X-ray-determined structure. The following distances (Å) and angles (deg) were used: Co–S = 2.23,

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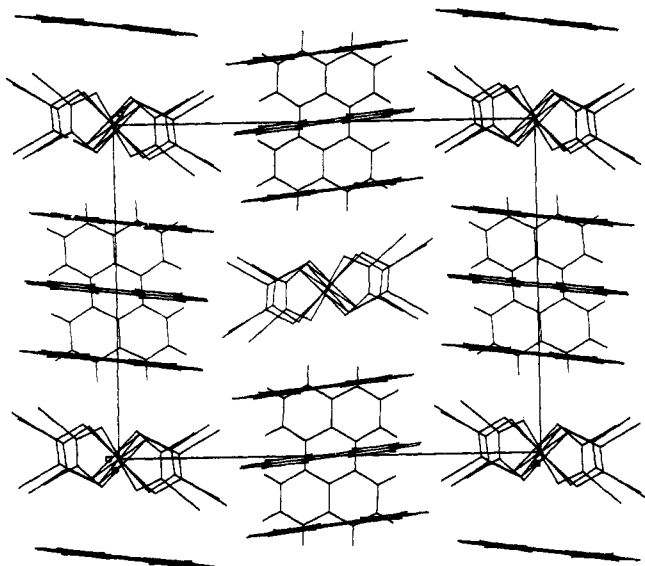(17) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

Table II. Final Fractional Atomic Coordinates and Equivalent Isotropic Thermal Displacement Parameters for Non-H Atoms with Esd's in Parentheses

	x	y	z	U_{eq} (Å^2)^a
		Residue 1		
Co(1)	0.00000(–)	0.00000(–)	0.00000(–)	0.0310(4)
Co(2)	–0.26420(8)	–0.00929(4)	0.01405(6)	0.0369(3)
S(1)	–0.03889(15)	0.06939(8)	–0.09913(10)	0.0361(6)
S(2)	–0.11838(15)	0.04949(8)	0.7382(10)	0.0356(6)
S(3)	–0.16048(16)	–0.06809(9)	–0.06013(11)	0.0416(6)
S(4)	–0.26517(17)	–0.08381(9)	0.10518(12)	0.0477(7)
S(5)	–0.38200(17)	0.04138(10)	0.08260(12)	0.0499(7)
S(6)	–0.32355(15)	0.04013(9)	–0.09539(11)	0.0417(6)
N(1)	–0.1376(7)	0.2362(3)	–0.1257(5)	0.077(3)
N(2)	–0.2303(8)	0.2141(4)	0.0973(5)	0.089(4)
N(3)	–0.0776(7)	–0.2382(3)	–0.0818(5)	0.075(3)
N(4)	–0.1923(7)	–0.2513(3)	0.1435(5)	0.082(3)
N(5)	–0.5716(6)	0.1776(4)	0.0733(5)	0.081(3)
N(6)	–0.4791(7)	0.1884(3)	–0.1567(5)	0.079(3)
C(1)	–0.986(6)	0.1309(3)	–0.0493(4)	0.037(3)
C(2)	–0.1204(6)	0.1896(3)	–0.0929(4)	0.044(3)
C(3)	–0.1329(6)	0.1234(3)	0.0263(4)	0.035(2)
C(4)	–0.1876(7)	0.1736(4)	0.0663(5)	0.054(3)
C(5)	–0.1603(6)	–0.1415(3)	–0.0119(4)	0.040(3)
C(6)	–0.1153(7)	–0.1953(4)	–0.0508(5)	0.050(3)
C(7)	–0.2030(6)	–0.1470(3)	0.0613(5)	0.043(3)
C(8)	–0.1974(7)	–0.2059(4)	0.1062(5)	0.055(3)
C(9)	–0.4344(6)	0.0983(3)	0.0179(4)	0.043(3)
C(10)	–0.5089(7)	0.1434(4)	0.0477(5)	0.053(3)
C(11)	–0.4055(6)	0.0990(3)	–0.0611(4)	0.040(3)
C(12)	–0.4478(7)	0.1487(4)	–0.1153(5)	0.055(3)
		Residue 2		
C(13)	0.4524(5)	0.4182(3)	0.1947(4)	0.036(2)
C(14)	0.3536(5)	0.4526(3)	0.2021(4)	0.036(2)
C(15)	0.3602(6)	0.5228(3)	0.2132(4)	0.036(2)
C(16)	0.4650(6)	0.5527(3)	0.2162(4)	0.036(2)
C(17)	0.5632(5)	0.5173(3)	0.2070(4)	0.038(3)
C(18)	0.5573(6)	0.4486(3)	0.1965(4)	0.036(2)
C(19)	0.2657(6)	0.5594(4)	0.2207(4)	0.049(3)
C(20)	0.2730(7)	0.6254(4)	0.2314(5)	0.057(3)
C(21)	0.3741(7)	0.6553(4)	0.2333(5)	0.051(3)
C(22)	0.4711(6)	0.6207(3)	0.2265(4)	0.043(3)
C(23)	0.5758(7)	0.6505(4)	0.2283(5)	0.055(3)
C(24)	0.6695(7)	0.6167(4)	0.2196(4)	0.053(3)
C(25)	0.6636(6)	0.5506(4)	0.2093(4)	0.047(3)
C(26)	0.6509(6)	0.4111(4)	0.1871(4)	0.047(3)
C(27)	0.6439(7)	0.3450(4)	0.1781(5)	0.054(3)
C(28)	0.5446(7)	0.3153(4)	0.1781(5)	0.054(3)
C(29)	0.4460(6)	0.3501(3)	0.1848(4)	0.043(3)
C(30)	0.3419(7)	0.3202(4)	0.1820(5)	0.055(3)
C(31)	0.2481(7)	0.3544(4)	0.1910(5)	0.053(3)
C(32)	0.2529(6)	0.4199(4)	0.1997(4)	0.045(3)
		Residue 3		
C(33)	0.0988(5)	0.0361(3)	0.04907(4)	0.034(2)
C(34)	–0.0053(6)	0.0670(3)	0.4896(4)	0.035(2)
C(35)	–0.1037(6)	0.0336(3)	0.4997(4)	0.036(2)
C(36)	–0.2048(6)	0.0665(4)	0.4992(4)	0.045(3)
C(37)	–0.2069(7)	0.1330(4)	0.4893(5)	0.053(3)
C(38)	–0.1130(6)	0.1657(4)	0.4795(4)	0.049(3)
C(39)	–0.0092(6)	0.1349(3)	0.4800(4)	0.042(3)
C(40)	0.0889(7)	0.1689(4)	0.4717(5)	0.055(3)
C(41)	0.1884(6)	0.1384(4)	0.4714(5)	0.052(3)
C(42)	0.1947(6)	0.0731(4)	0.4802(4)	0.048(3)
		Residue 4		
C(43)	0.5175(5)	–0.0578(4)	0.4547(4)	0.041(3)
C(44)	0.5156(5)	0.0038(4)	0.4157(4)	0.040(2)
C(45)	0.4994(6)	0.0609(3)	0.4584(4)	0.042(3)
C(46)	0.4993(6)	0.1186(4)	0.4177(5)	0.054(3)
C(47)	0.5155(6)	0.1209(4)	0.3363(5)	0.060(3)
C(48)	0.5313(6)	0.0668(5)	0.2945(5)	0.061(3)
C(49)	0.5327(5)	0.0057(4)	0.3321(5)	0.050(3)
C(50)	0.5469(6)	–0.0507(5)	0.2890(5)	0.060(3)
C(51)	0.5503(6)	–0.1074(5)	0.3268(5)	0.064(4)
C(52)	0.5340(6)	–0.1119(4)	0.4100(5)	0.054(3)

^{a} $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a_j$.

S–C = 1.72, C–C = 1.44, C–N = 1.14, C=C = 1.33, S–Co–S = 90. The interunit distances are given in the text.

Figure 1. Projection of the (Per)$_4$[Co(mnt)$_2$]$_3$ crystal structure along the *a* axis.

Table III. Selected Bond Distances (Å) and Angles (deg)

Co(1)–S(1)	2.2202(17)	N(2)–C(4)	1.136(12)
Co(1)–S(2)	2.2116(17)	N(3)–C(6)	1.146(11)
Co(1)–S(3)	2.5502(19)	N(4)–C(8)	1.133(11)
Co(2)–S(2)	2.312(2)	N(5)–C(10)	1.147(12)
Co(2)–S(3)	2.200(2)	N(6)–C(12)	1.126(11)
Co(2)–S(4)	2.175(2)	C(1)–C(2)	1.440(9)
Co(2)–S(5)	2.167(2)	C(1)–C(3)	1.362(10)
Co(2)–S(6)	2.168(2)	C(3)–C(4)	1.431(11)
S(1)–C(1)	1.718(7)	C(5)–C(6)	1.426(11)
S(2)–C(3)	1.739(7)	C(5)–C(7)	1.362(11)
S(3)–C(5)	1.732(7)	C(7)–C(8)	1.439(11)
S(4)–C(7)	1.711(7)	C(9)–C(10)	1.419(11)
S(5)–C(9)	1.695(7)	C(9)–C(11)	1.385(9)
S(6)–C(11)	1.705(7)	C(11)–C(12)	1.444(11)
N(1)–C(2)	1.129(9)		

S(1)–Co(1)–S(2)	89.80(6)	S(1a)–Co(1)–S(2a)	89.80(6)
S(1)–Co(1)–S(3)	87.76(6)	S(1a)–Co(1)–S(3a)	87.76(6)
S(1)–Co(1)–S(1a)	180(–)	S(2a)–Co(1)–S(3a)	88.50(6)
S(1)–Co(1)–S(2a)	90.20(6)	S(2)–Co(2)–S(3)	95.15(8)
S(1)–Co(1)–S(3a)	92.24(6)	S(2)–Co(2)–S(4)	97.18(8)
S(2)–Co(1)–S(3)	88.50(6)	S(2)–Co(2)–S(5)	91.38(8)
S(2)–Co(1)–S(1a)	90.20(6)	S(2)–Co(2)–S(6)	107.55(7)
S(2)–Co(1)–S(2a)	180(–)	S(3)–Co(2)–S(4)	91.34(8)
S(2)–Co(1)–S(3a)	91.50(6)	S(3)–Co(2)–S(5)	173.40(9)
S(3)–Co(1)–S(1a)	92.24(6)	S(3)–Co(2)–S(6)	87.84(8)
S(3)–Co(1)–S(2a)	91.50(6)	S(4)–Co(2)–S(5)	86.88(8)
S(3)–Co(1)–S(3a)	180(–)	S(4)–Co(2)–S(6)	155.24(9)
S(3)–Co(1)–S(3a)	180(–)	S(5)–Co(2)–S(6)	91.11(8)

Standard parameters were used for C, N, S, and H, while those for Co were the following ($-H_{ii}$/eV, ζ): 4s 9.21, 2.00; 4p 5.29, 2.00; 3d 13.18, 5.55; 0.5679 (C_1), 2.10 (ζ_2), 0.6059 (C_2). The three-dimensional molecular orbital drawings were made using the program CACAO.[18]

Results and Discussion

The crystal structure consists of mixed stacks of perylene trimers alternating with individual perylene molecules, almost perpendicular to the trimers, and stacks of [Co(mnt)$_2$]$_3$ units; both stacks extend along *a* and alternate in the *bc* plane, as shown in Figure 1. In the unit cell there are three independent perylene units. A full molecule (residue 2) is the outer molecule of a centrosymmetric stacked perylene trimer, a half one (residue 3) is the central unit of this trimer located on an inversion center, and one other half molecule (residue 4) refers to an isolated molecule almost perpendicular to this trimer and located on another inversion
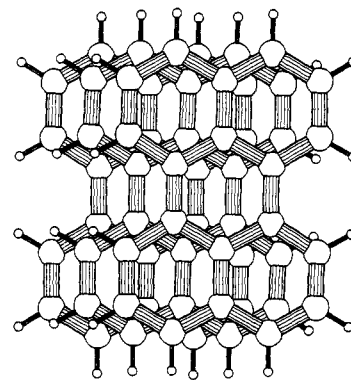
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Figure 2. Projection of the perylene trimer perpendicular to the plane of the central molecule.
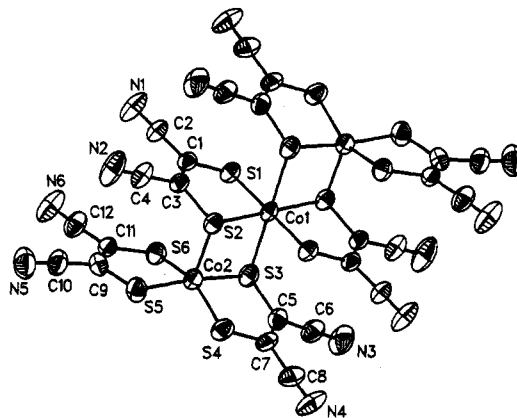

Figure 3. ORTEP drawing of the trinuclear Co complex and the adopted numbering scheme.

center. Within experimental uncertainty, all perylene molecules are planar and have identical bond lengths.

The perylene molecules in a trimer are almost parallel, and their stacking mode is shown in Figure 2. The centers of gravity of the outer molecules of the perylene trimer (residue 2) are 3.362(6) Å from the plane of the central molecule (residue 3). The outer molecules of the perylene trimer form an angle of 1.3(1)° with the central one. As a consequence the distance of the centroid of the central perylene molecule, which is also an inversion center, to the plane of the outer perylene molecules is 3.383(6) Å. The average interplanar distance of the perylene molecules in the trimer (3.37 Å) is significantly shorter than that observed in the neutral molecule (3.47 Å),[19] thus indicating a significant interaction. It should be noted however that this distance in (Per)$_4$[Co(mnt)$_2$]$_3$ is not as short as those observed in the conducting compounds (Per)$_n$M(mnt)$_2$, where perylene molecules are stacked in a strictly parallel fashion but show a different overlap mode with interplanar distances slightly shorter than the average distance in this case (3.28 Å for M = Co with n = 1,[2] 3.32–3.36 Å in cases with n = 2[1,20–22]).

The trinuclear Co complex is shown in Figure 3. The central Co atom is placed at an inversion center, and the central Co(mnt)$_2$ unit has a slight distortion toward a chairlike conformation. The units above and below are significantly more distorted in a fashion that allows a short Co–S distance and larger distances between the ligands. As can be observed in Table IV, where the Co–S bond distances in several Co–bis(dithiolene) complexes

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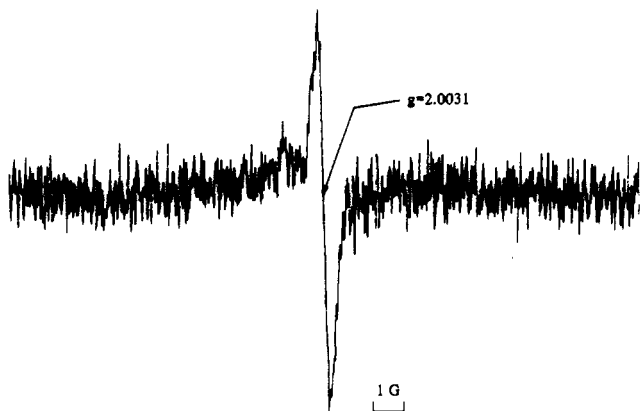(21) Domingos, A.; Henriques, R. T.; Gama, V. P.; Almeida, M.; Lopes Vieira, A.; Alcácer, L. *Synth. Met.* **1989**, *27*, B411.

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Table IV. Co–S Bond Lengths (Å) in Different Co–Bis(dithiolene) Complexes

	$Co(mnt)_2^{2-}$ [a]	$Co_2(S_2C_2(CF_3)_2)_4^0$ [b]	$Co_2(S_2C_6Cl_4)_4^{2-}$ [c]	$[Co(mnt)_2]_n$ [d]	$[Co(mnt)_2]_3^-$ [e] central	$[Co(mnt)_2]_3^-$ [e] outer
equatorial	2.16	2.16(2)	2.185(7)	2.237(7)	2.2116(17)	2.200(2)
				2.224(7)	2.2202(17)	2.175(2)
				2.232(7)		2.167(2)
				2.225(7)		2.168(2)
apical		2.38(4)	2.404(7)	2.443(9)	2.5502(19)	2.312(2)
				2.62(1)		

[a] Reference 24. [b] Reference 4. [c] Reference 3. [d] Reference 2. [e] This work.

Figure 4. X-Band EPR spectrum of (Per)₄[Co(mnt)₂]₃ crystals at 300K.

Figure 5. View of the trimer in the real structure emphasizing the distortion around the Co atoms.

are compared, the Co–S apical distances are very different for the central and outer units. While the central Co atom achieves a distorted octahedral coordination with two long apical Co–S bonds (2.5502(19) Å), only surpassed in length by one of those of the zigzag chain polymer (Per)Co(mnt)₂(CH₂Cl₂)₀.₅, the outer Co atoms are pentacoordinated; the Co–S apical bond (2.312(2) Å) is shorter here than those found in dimerized compounds (2.38–2.40 Å). A slight extension of the Co–S equatorial bonds in the central cobalt atom (2.211–2.220 Å) is observed relative to those of the outer cobalt atoms (2.20–2.16 Å). The latter are of the same order as those found previously in dimeric Co–bis(dithiolene) complexes. This behavior may be assigned to the considerable distortion found in the trimer. In order to achieve better bonding between Co(mnt)₂ units, the bonding within Co(mnt)₂ must become weaker.

The EPR spectrum of five randomly aligned single crystals of (Per)₄[Co(mnt)₂]₃ at room temperature (Figure 4) presents only a narrow (0.4 G) line at $g = 2.0031$. The isotropic nature of this g value, within 10^{-4}, was confirmed both by the narrowness of the line and by the absence of significant g shifts upon sample rotation in the cavity.

To the best of our knowledge, the present structure represents the first example of a trinuclear species based on M(mnt)₂, the only similarly puckered trimer of bis(dithiolenes) previously described being [Ni(dddt)₂]₃²⁺ (dddt = 5,6-dihydro-1,4-dithiin-2,3-dithiolate).[23] The present arrangement of Co(mnt)₂ units in a trimer, the square planar mononuclear complexes,[24] the dimeric species with square pyramidal coordination,[3,4] and the polymeric one[2] demonstrate the variability of structural arrangements of Co–bis(dithiolene) molecules. The arrangement of the perylene molecules, although complex, is not too surprising in view of previously reported widely variable structures in other perylene compounds.[25]

The general packing mode with alternating perylene and [Co-
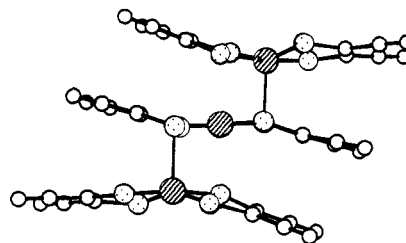
(mnt)₂]₃ molecules indicates a charge transfer whose characterization is one of the most interesting aspects of this compound. Although electrical conductivity was not measured in single crystals (too small to make electrical contacts), the existence of isolated units in the structure, without a pathway for delocalizing interactions, does not allow electrical conductivity and the crystals are expected to be insulators. This would not favor their growth directly on the electrode, and most likely the compound is a thermodynamically more stable product, resulting from secondary decomposition reactions of the conducting species (Per)Co(mnt)₂-(CH₂Cl₂)₀.₅ and (Per)₂Co(mnt)₂, which are probably kinetically favored products formed on the electrode surface. The diversity of products in this electrochemical preparation results from the previously described[2] proximity of the oxidation potentials of perylene (0.92 V vs SCE) and of [Co(mnt)₂]₂²⁻ (to that of [Co(mnt)₂]₂⁻, 0.88 V vs SCE). Under the preparative conditions used, several oxidation reactions occur, thus leading to different mixed-valence compounds.

A discussion of the factors that control the extended range of molecular arrangements found in Co(mnt)₂ compounds will be published elsewhere.[26] In the present study, molecular orbital calculations of the extended Hückel type[16] were used to understand this particular geometry and the extent of charge transfer between the organic and the inorganic fragments. A molecular approach was used, because [Co(mnt)₂]₃ and (Per)₃ have no close contacts between them and to the isolated fourth perylene molecule in the unit cell.

The inorganic trimer, [Co(mnt)₂]₃*⁻, is constructed by putting together three square planar units and allowing them to distort: the central one achieves a slight chair conformation, with the Co and the four S atoms in the same plane, while in the two outer ones there is a significant pyramidalization around the Co (Figure 5).

In a typical Co(III) d⁶ square planar complex, [Co(mnt)₂]⁻, the interaction between the metal and the sulfur ligands is very similar to that described for [Ni(S₂C₂H₂)₂],[27] with a four below one splitting of the d levels (figure 6). Three of the d levels are occupied as well as the levels corresponding to the sulfur lone pairs. In this description 3b₂g was considered as "the xz" orbital. The complete story is that there is considerable mixing between all the b₂g orbitals, 2b₂g also has significant xz character, and the real composition may be parameter dependent. Using this bonding

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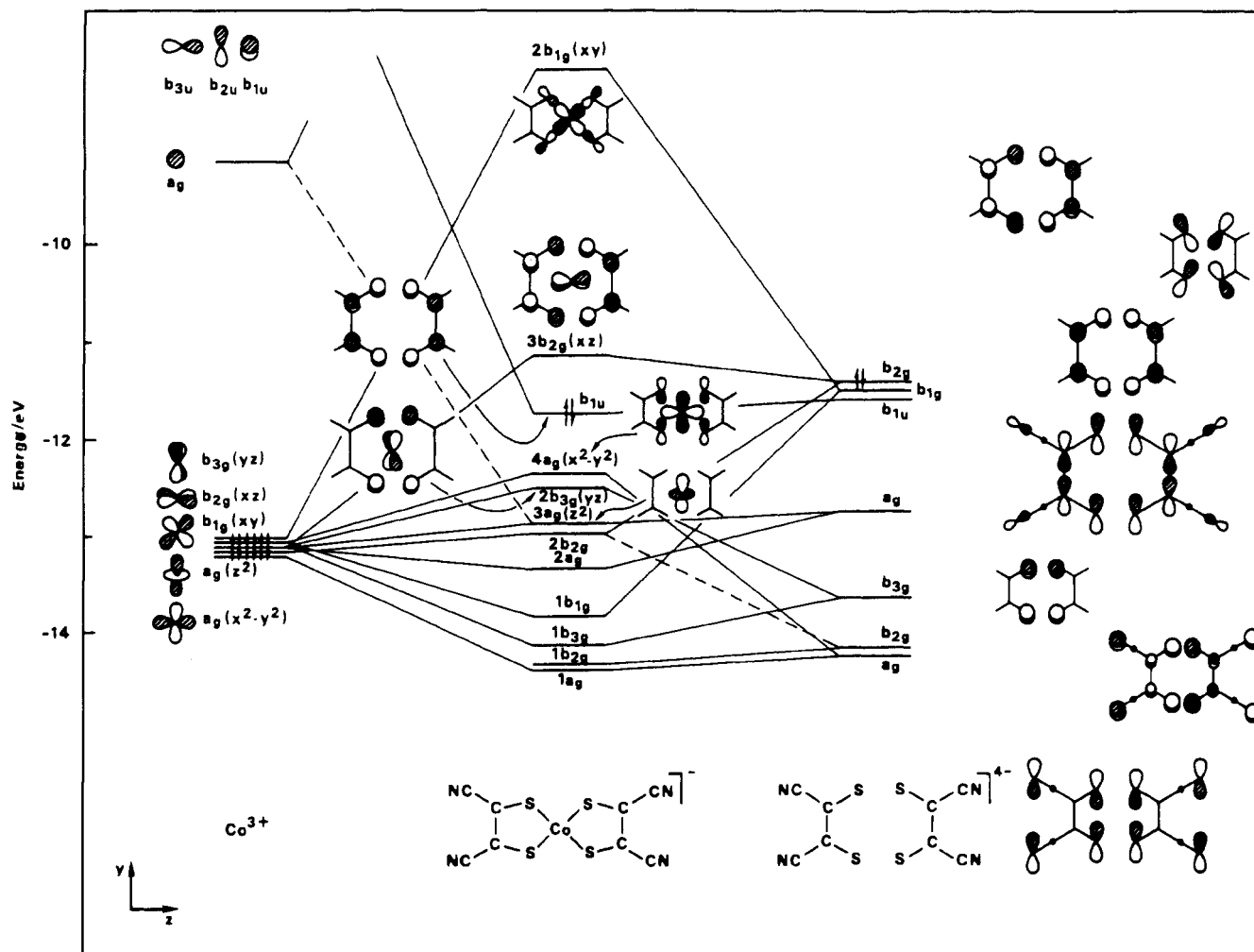(27) Alvarez, S.; Vicente, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 6253.

Figure 6. Interaction diagram for Co(III) and two mnt ligands.

model, in the formally d^7 [Co(mnt)$_2$]$^{2-}$ anion, with slightly distorted square planar geometry,[24] the extra electron occupies xz and there are seven d electrons. For the model Co(III) complex, the HOMO is essentially located on the CSSC atoms of each ligand and resembles the LUMO of butadiene. In the coordinate system chosen, the highest d level is xy^*.

A first step toward modeling the real structure consists of assembling the trimer. The distance between planar [Co(mnt)$_2$]$^-$ units is taken as 2.31 Å (apical Co–S bond of the outer cobalt atoms). The Co atom of each outer unit is directly above or below one sulfur of the central one (Figure 7a). This model trimer has a much higher energy (17.5 eV) than the real trimer, and there is a net antibonding interaction between the three molecules. This can be assigned to strong repulsions between filled levels of adjacent molecules, namely sulfur and nitrogen of the central unit and carbons of the outer units. This type of four-electron destabilizing interaction can be observed, for instance, in the HOMO of [Co(mnt)$_2$]$_3$$^{3-}$, which is antibonding between those atoms, as sketched in Figure 7b, where, for simplicity, only the largest contributions to this orbital are shown.

This model describes well the effects of changing the coordination number of the cobalt atoms from 4 to 5 (outer cobalts) or 6 (central cobalt). The overlap populations are indicative of bond strengths (Co$_{central}$–S$_{ap}$ = 0.297, Co$_{outer}$–S$_{ap}$ = 0.217). However, this model is not realistic because too many repulsive interactions between the mnt ligands arise simultaneously. A distortion is needed to relieve them, at least partially. We allowed the central molecule to approach a chair conformation while allowing the other ones to approach a pyramidal coordination, keeping all mnt groups planar.
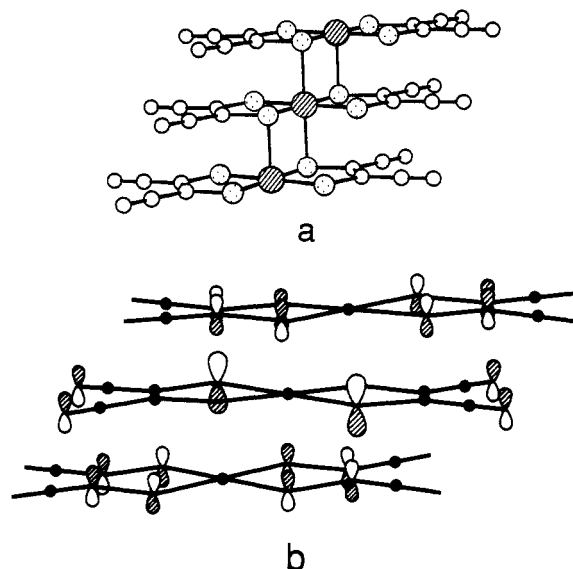

Figure 7. (a) Trimer model with planar parallel Co(mnt)$_2$ units at 2.3 Å. (b) The corresponding HOMO.

The structure is now close to that of the real trimer (Figure 5), and the energy drops accordingly. The atoms responsible for the repulsions are now further apart (S···S, S···C). On the other hand, and in spite of some mixing that takes place as the symmetry is lowered, the energies of the molecular orbitals in each distorted [Co(mnt)$_2$]$^-$ unit do not significantly differ from those of the undistorted species.

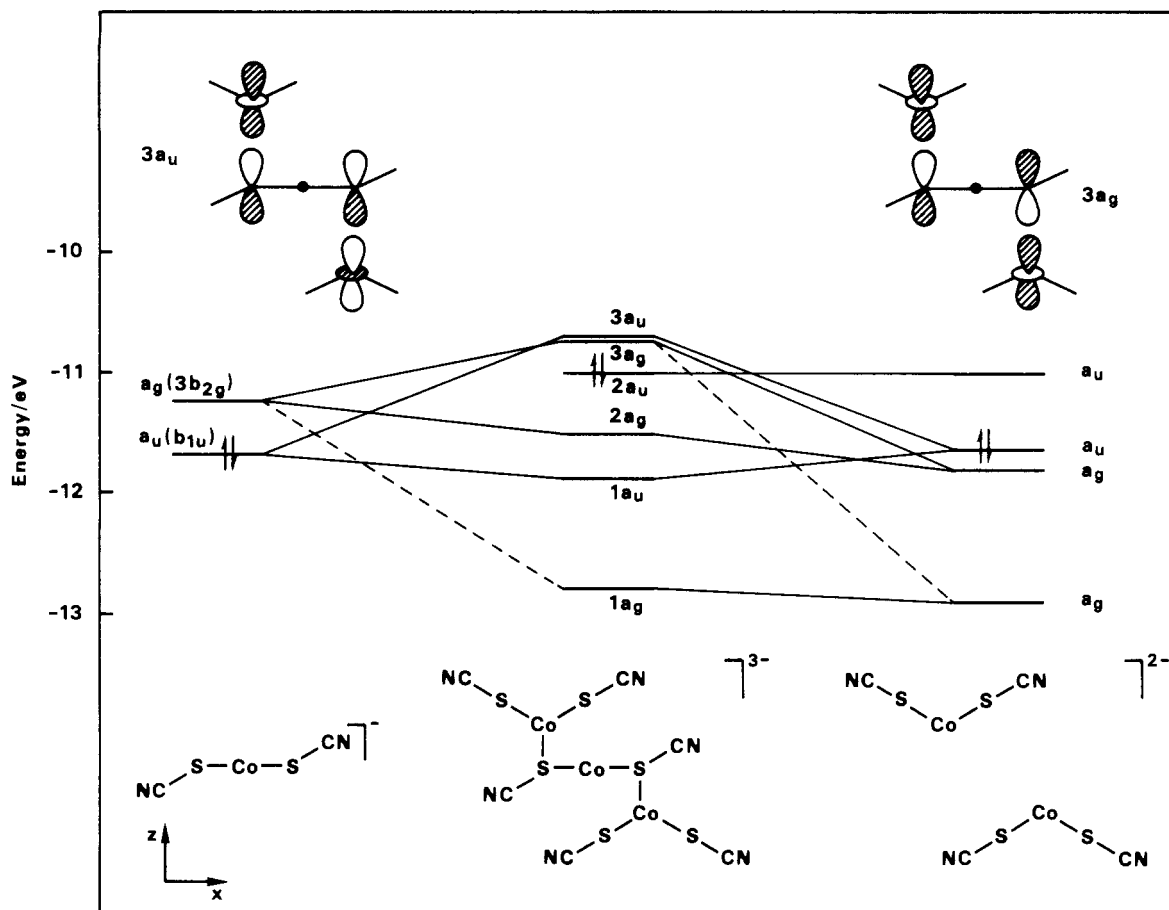**Figure 8.** The more important interactions between adjacent molecules in the $[Co(mnt)_2]_3$ trimer and its frontier orbitals.

As a matter of fact, when the bonding is analyzed, it can be seen that the four-electron repulsive interactions have disappeared and a strong bonding overlap population exists between the central and the outer molecules. The HOMO, shown in Figure 7b for the first model, has now a nonbonding character, with almost no contribution from the middle molecule, comparable to the nonbonding level in a π-allylic system. What keeps the three molecules together are the new Co–S bonds formed (overlap populations are now $Co_{central}$–$S_{ap} = 0.066$ and Co_{outer}–$S_{ap} = 0.346$). The $Co_{central}$–S_{ap} bonds are much weaker in this model, because the distortion forced the S atoms to move away from the central Co (the Co–S distance is now 2.85 Å). In order to reproduce the real structure, the two S atoms needed by this cobalt atom to complete its hexacoordination have to move closer (Co–S becomes 2.55 Å). The corresponding overlap population increases to 0.339. On the other hand, the ligand becomes nonplanar with this movement, as experimentally observed. In spite of this small discrepancy, the model seems to describe adequately the behavior of the real trimer and is very close to it in energy (0.6 eV).

The molecular orbital diagram for the trimer is too complicated to describe; an outline of the interactions leading to the formation of the Co–S_{ap} bonds is given in Figure 8, which includes the frontier orbitals. They involve empty z orbitals of sulfur and z^2 orbitals of cobalt in the nearby molecules, while weaker π destabilizing interactions between yz and y also take place.

It is interesting that a change in electron count from $[Co(mnt)_2]_3^{3-}$ (only Co(III), d^6) to $[Co(mnt)_2]_3^-$ (formally one Co(III) and two Co(IV)) to keep the molecule diamagnetic does not significantly affect the overlap populations quoted. The reason is that the HOMO of the Co(III) trimer ($2a_u$ in Figure 8) is an essentially intratrimer nonbonding orbital significantly centered on the cobalts of the two outer molecules. Upon oxidation, the two electrons will come from them, which means that the central molecule should contain formally Co(III), while Co(IV) would

be present in each of the outer molecules. Before discussing further the electron count, however, it is convenient to understand what is happening with the organic trimer.

The perylene molecule is well-known for its ability to oxidize and to form segregated stacks that can lead to high electrical conductivity[1,2,20–22] or to form molecular aggregates[24] (dimers, trimers, etc.) by combination with appropriate acceptors. Only the π orbitals will be relevant for such types of interactions between perylene molecules. Different stacking patterns are possible depending on the slipping direction.

Although slipping along x has been found in $(Per)_nM(mnt)_2$ compounds,[1,2,20–22] in this particular trimer it is found instead that each molecule has slipped 0.988 Å along y with an insignificant shift (less than 0.01 Å) along x and with a very small (1.3° about x) tilt of the outer molecules relative to the central one.

In a first step, a trimer was assembled from three parallel molecules at a 3.37-Å distance. However, its energy was higher than 3 times the energy of each isolated molecule and no attractive interactions were detected. Upon removal of one electron, the trimer was stabilized. The HOMO of the trimer is the antibonding orbital resulting from interaction of the $2a_u$ orbital (shown in Figure 9) on the neutral perylene and the antisymmetric combination of the same π orbital in the two outer perylenes. In the monocationic trimer it is half-filled.

The same pattern is observed for the real structure of the perylene trimer, where the outer molecules are slightly tilted toward the central one so that a better contact in the central part of the trimer is achieved while the outer part is separated. This small deviation is sufficient to relieve most of the small repulsive interactions between adjacent molecules, in a fashion similar to, but to a smaller extent than, that found for the inorganic trimer.

The almost isotropic EPR line of $(Per)_4[Co(mnt)_2]_3$ is ascribed to an unpaired electron in the organic fragments, either Per^+ or
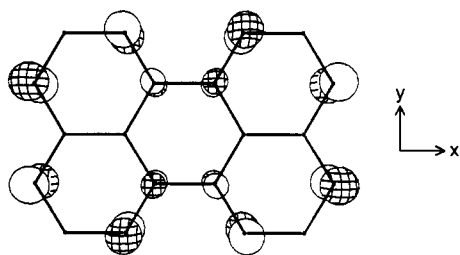
Figure 9. HOMO of the neutral perylene molecule.

most probably $(Per)_3^+$. In the case of a paramagnetic organometallic species, an anisotropic line would be expected but, if too large, it would become difficult to detect, and therefore from EPR data alone $[Co(mnt)_2]_3^{2-}$ cannot be excluded. However the MO calculations suggest that a more stable configuration would be expected for $[Co(mnt)_2]_3^-$ than for $[Co(mnt)_2]_3^{2-}$. Indeed, for that situation, the trimer should be diamagnetic, with the three cobalts formally in oxidation states IV, III, and IV, exactly the electron count referred to above. Considering that the two electrons "removed" from the "all Co(III)" species belonged to a relatively high energy molecular orbital, not contributing to the interunit bonding, it is not surprising that it remains empty. The HOMO–LUMO gap in the trimer is wider for the lower electron count than for the higher one. In addition, although the calculations cannot be taken quantitatively, it is worth noting that the donor orbital has a higher energy than the acceptor one. In this case, the transferred electron should come preferentially from $(Per)_3$ rather than from the isolated perylene molecule. We therefore suggest the formulation of this compound as $(Per)_3^+$-$(Per)^0[Co(mnt)_2]_3^-$.