# The Crystal and Molecular Structure of the Tetra-*n*-butylammonium Salt of the Dianionic Dimer of Bis(1,2,3,4-tetrachlorobenzene-5,6-dithiolato)cobaltate

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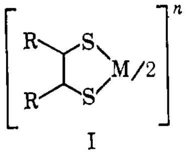
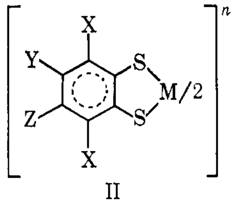
**Abstract:** The crystal and molecular structure of the tetra-*n*-butylammonium salt of the dimer of the bis(1,2,3,4-tetrachlorobenzene-5,6-dithiolato)cobaltate anion has been determined from three-dimensional single-crystal X-ray data collected by film methods. The structure has been refined by least-squares procedures to conventional and weighted $R$ factors of 0.094 and 0.080, respectively, for 1588 nonzero reflections. The complex crystallizes in space group $P2_1/c$-$C_{2h}{}^5$ of the monoclinic system in a unit cell of dimensions: $a = 13.95 \pm 0.03$, $b = 18.98 \pm 0.04$, $c = 15.36 \pm 0.03$ Å, $\beta = 114.8 \pm 0.4°$, and $V = 3692$ Å$^3$. An experimental density of $1.52 \pm 0.05$ g/cm$^3$ agrees well with a calculated value of 1.54 g/cm$^3$ for two dimeric molecules in the unit cell. The $[Co_2(S_2C_6Cl_4)_4]^{2-}$ dimer units are centrosymmetric with the center of symmetry at the origin located midway between the Co atoms. Dimerization occurs through the formation of two Co–S bonds of length 2.404 Å, making each Co atom five-coordinate. The estimated standard deviation for this Co–S distance is 0.007 Å. The coordination about the Co atom is best described as square pyramidal with the metal atom raised 0.26 Å out of the plane of the four basal S atoms toward the apical S of the second planar unit. The $[Co(S_2C_6Cl_4)_2]^-$ half-dimer unit is only approximately planar with the ends of the benzene rings bent out of the plane, presumably because of repulsion effects from the adjacent half-dimer unit. Molecular orbital calculations on related Ni systems are used to provide an electronic explanation for the dimerization of the $[Co(S_2C_6Cl_4)_2]^-$ units. The electronegative chlorine substituents remove electron density from the central metal atom, particularly that associated with the metal $4p_z$ orbital; the $4p_z$ is thus available for forming axial $\sigma$ bonds with electron donor groups. The intermonomer bonding in the $[Co_2(S_2C_6Cl_4)_4]^{2-}$ dimer unit is attributed to two $\sigma$ bonds formed between the Co $4p_z$ orbitals and occupied $\pi$ orbitals which have large S components.

The remarkable stability of square-planar transition metal complexes containing unsaturated five-membered metal chelate rings with sulfur donor atoms is well established.[2] Recent studies aimed at the elucidation of the electronic structures of complexes of types I and II have indicated that the electronic nature of the substituent plays an important role in stabilizing these systems and in influencing their magnetic behavior.[3]



I

$R = CN, CF_3, C_6H_5, CH_3, H$



II

$X = Y = Z = H, CH_3, Cl$[4]

$X = Y = H; Z = CH_3$

$X = H; Y = Z = CH_3$

This influence can be seen by comparing the magnetic properties of two closely related monoanionic Co complexes. The bis(toluene-3,4-dithiolato)cobaltate complex has been found to have a stable spin-triplet ground state in both the solid and solution states for a wide variety of solvents.[5] Similar magnetic behavior has been observed for the related $Co(bdt)_2^-$, $Co(xdt)_2^-$, and $Co(pdt)_2^-$ complexes.[3] In contrast, the bis(1,2,3,4-tetrachlorobenzene-5,6-dithiolato)cobaltate complex is diamagnetic in the solid state and exhibits varying magnetic behavior in solution, depending on the coordinating ability of the solvent. In poorly coordinating solvents, such as cyclohexane and tetrahydrofuran, $Co(S_2C_6Cl_4)_2^-$ is paramagnetic with magnetic moments indicating a full spin-triplet ground state ($\mu_{eff} = 3.14$ and 3.18 BM, respectively). In the stronger coordinating solvent, dimethyl sulfoxide, the magnetic moment is reduced to a value of 2.37 BM. In pyridine, a very strong coordinating solvent, $Co(S_2C_6Cl_4)_2^-$ is diamagnetic and there is evidence for addition of pyridine to give five- and six-coordinate species.

The unusual magnetic properties of $Co(S_2C_6Cl_4)_2^-$ can be explained in several different ways. First, it is possible that the spin-singlet ground state in the solid results from a sufficiently large separation of the highest occupied and lowest unoccupied energy levels in monomer units; the levels may then be significantly perturbed in solution to give a spin-triplet monomer species. A second possibility is the existence of strong pairwise interactions between spin-triplet monomer

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[2] (a) E. Billig, R. Williams, I. Bernal, J. H. Waters, and H. B. Gray, *Inorg. Chem.*, 3, 663 (1964); (b) G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 87, 3585 (1965); (c) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 2, 1277 (1963).

[3] M. J. Baker-Hawkes, E. Billig, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 4870 (1966).

[4] The following abbreviations are used to denote the respective ligand systems: bdt = benzene-1,2-dithiolate, X = Y = Z = H; tdt = toluene-3,4-dithiolate, X = Y = H, Z = $CH_3$; xdt = xylene-4,5-dithiolate, X = H, Y = Z = $CH_3$; and pdt = prehnitene-5,6-dithiolate, X = Y = Z = $CH_3$.

[5] R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 43 (1966).

units in the solid resulting in diamagnetism. This possibility has been partially realized in the monoanionic complex bis(maleonitriledithiolato)nickelate (I with R = CN). The reduced magnetic moment observed for this complex in the solid state ($\mu_{\text{eff}} \sim 1.0$ BM) has been shown to result from magnetic interactions between pairs of nearby planar anion units.[6] In the extreme, strong pairwise interactions can lead to structurally identifiable dimeric species in the solid state. The neutral bis(*cis*-1,2-trifluoromethylethene-1,2-dithiolato)cobalt complex has been shown to have a dimeric structure.[7] Thus, the effect of the crystalline coordination environment on the various Co systems must be unequivocally established before any meaningful conclusions about their electronic structures can be made.

The present study is the second part of our investigations on the structures of monoanionic cobalt complexes. In the first paper, the results of a structure determination on the triphenylmethylarsonium bis(toluene-3,4-dithiolato)cobaltate complex were presented.[8] The $Co(tdt)_2^-$ anions were found to be essentially square planar with the anion units well separated (Co–Co distance 10.21 Å). The spin-triplet ground state was explained in terms of two close-lying out-of-plane $\pi$ orbitals.[9]

In this paper, we present the results of an X-ray structure determination on the tetra-*n*-butylammonium salt of the bis(1,2,3,4-tetrachlorobenzene-5,6-dithiolato)cobaltate complex. This structure determination confirms the existence of a dimeric anion in the solid state. A comparison of the structure with related Co structures is presented, and a model is proposed for the electronic nature of intermonomer bonding in the dimeric structures.

**Unit Cell and Space Group Determination.** The complex $[(n\text{-}C_4H_9)_4N]_2[Co_2(S_2C_6Cl_4)_4]$ was synthesized according to the procedure previously described[3] and shiny blue-black crystals of the complex were obtained by recrystallization from methylene chloride solution. On the basis of precession and Weissenberg photographs taken with Mo K$\alpha$ radiation, the crystals were found to belong to the monoclinic system. The cell has the dimensions: $a = 13.95 \pm 0.03$, $b = 18.98 \pm 0.04$, $c = 15.36 \pm 0.03$ Å, $\beta = 114.8 \pm 0.4°$, $V = 3692$ Å$^3$. An experimental density of $1.52 \pm 0.05$ g/cm$^3$, obtained by the flotation method using a mixture of hexane and carbon tetrachloride, is in good agreement with a density of 1.54 g/cm$^3$ calculated from the X-ray data for four monomeric molecules or two dimeric units in the unit cell. The systematic extinctions, 0*k*0 for *k* odd and *h*0*l* for *l* odd, indicate the centrosymmetric space group $C_{2h}^5$-$P2_1/c$ and thus imply the probability that all atoms for one monomeric unit are in general positions of the space group. However, crystallographic symmetry conditions impose a center of symmetry on the dimer.

**Collection and Reduction of the X-Ray Data.** Intensity data were collected at room temperature by the multiple film equiinclination Weissenberg technique, using Zr-filtered Mo K$\alpha$ radiation. The crystal was mounted with *a* as the rotation axis, and the layers 0*kl* to 8*kl* were recorded. The intensities of 2921 independent reflections accessible within the angular range $\theta_{\text{Mo}} < 20°$ were estimated visually from a calibrated intensity strip. The usual Lorentz-polarization factors were then applied to the intensities to yield $F_o^2$ values (where $F_o$ is the observed structure amplitude). The $F_o$ values were subsequently brought to an approximate absolute scale using a modification of Wilson's statistical method. No corrections were made for absorption due to the small size of both the crystal (a parallelepiped of approximate dimensions 0.13 × 0.10 × 0.08 mm) and the linear absorption coefficient ($\mu = 12.7$ cm$^{-1}$ for Mo K$\alpha$ radiation).

**Solution and Refinement of the Structure.** The positions of the cobalt and two sulfur atoms were determined from a three-dimensional Patterson function[10] after much trial and error. The structure proved difficult to solve because of the large number of heavy atoms in the unit cell which resulted in many Patterson peaks of relatively high density. A three-dimensional difference Fourier based on phases obtained from these Co and S atom positions yielded the locations of one Cl and an additional S atom. The positions of the remaining S and seven Cl atoms were then determined from a second difference Fourier map. The positions of all 28 carbon atoms and the one cation nitrogen were located in subsequent difference Fourier maps based on phases obtained from the refined positions of the heavy atoms.

The structure was refined by a least-squares procedure. The function minimized was $\Sigma w(F_o - F_c)^2$, where the weights $w$ were assigned in the following way: $I < 4$, $w = (I/4)^2$; $4 < I < 175$, $w = 1$; $I > 175$, $w = (175/I)^2$, $I$ being the average raw intensity for the particular reflection. The atomic scattering factors for the neutral atoms tabulated by Ibers[11a] were used. The anomalous parts of the Co, S, and Cl scattering factors were obtained from Templeton's tabulation[11b] and were included in the calculated structure factors.

Initially, the refinement was carried out in which all atoms were assigned individual isotropic thermal parameters. This refinement of 177 positional, scale, and thermal parameters converged to a conventional $R$ factor ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.138 and a weighted $R$ factor $R'$ ($R' = (\Sigma w(F_o - F_c)^2/\Sigma wF_o^2)^{1/2}$) of 0.136. A difference Fourier based on this refinement provided evidence for considerable anisotropic thermal motion of the heavy atoms.

After the correction of several indexing errors, a final refinement was carried out in which the Co, S, and Cl atoms were allowed to vibrate anisotropically. In this refinement, the 12 independent C atoms of the anion, together with the 17 C and N atoms of the $(n\text{-}C_4H_9)_4N^+$ cation, were restricted to isotropic vibration. Because of computer limitations, this partial anisotropic refinement was carried out in blocks. First the positional and thermal parameters of the

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(6) J. F. Weiher, R. R. Melby, and R. E. Benson, *J. Am. Chem. Soc.*, **86**, 4329 (1964).

(7) J. H. Enemark and W. H. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).

(8) R. Eisenberg, Z. Dori, H. B. Gray, and J. A. Ibers, *ibid.*, **7**, 741 (1968).

(9) M. J. Baker-Hawkes, Ph.D. Thesis, Columbia University, 1967.

(10) In addition to various local programs, the main programs for the IBM 7094 computer used in this work were local modifications of Zalkin's FORDAP Fourier program and the Busing-Levy ORFLS least-squares program. C. K. Johnson's ORTEP Thermal Ellipsoid Plotting Program was used for the illustrations.

(11) (a) J. A. Ibers, "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1; (b) D. H. Templeton, *ibid.*, Table 3.3.2.

**Table I.** Final Parameters for $[(n\text{-}C_4H_9)_4N]_2[Co_2(S_2C_6Cl_4)_4]$

| Final Positional and Isotropic Thermal Parameters | | | | |
|---|---|---|---|---|
| Atom | *x* | *y* | *z* | *B*, Å$^2$ |
| Co | 0.0651 (3)[a] | 0.0571 (2) | −0.0237 (2) | 4.0 (1)[b] |
| S$_1$ | 0.1932 (6) | 0.1294 (3) | 0.0581 (4) | 5.1 (3)[b] |
| S$_2$ | 0.1757 (5) | −0.0114 (3) | −0.0488 (4) | 5.0 (3)[b] |
| S$_3$ | −0.0604 (5) | −0.0114 (3) | −0.1205 (3) | 3.5 (2)[b] |
| S$_4$ | −0.0493 (5) | 0.1433 (3) | −0.0472 (4) | 4.7 (3)[b] |
| Cl$_1$ | −0.2644 (5) | −0.0621 (3) | −0.2969 (4) | 5.2 (3)[b] |
| Cl$_2$ | −0.4697 (6) | 0.0255 (3) | −0.3675 (4) | 7.0 (3)[b] |
| Cl$_3$ | −0.4673 (6) | 0.1697 (4) | −0.2723 (5) | 8.3 (4)[b] |
| Cl$_4$ | −0.2581 (6) | 0.2317 (3) | −0.1194 (4) | 7.7 (3)[b] |
| Cl$_5$ | 0.4142 (6) | 0.1815 (3) | 0.2099 (4) | 7.9 (4)[b] |
| Cl$_6$ | 0.6155 (6) | 0.0933 (5) | 0.2512 (5) | 8.9 (4)[b] |
| Cl$_7$ | 0.5982 (6) | −0.0487 (4) | 0.1484 (5) | 8.7 (4)[b] |
| Cl$_8$ | 0.3796 (6) | −0.1015 (4) | −0.0017 (4) | 7.2 (3)[b] |
| C$_1$ | −0.176 (2) | 0.042 (1) | −0.170 (1) | 4.1 (5) |
| C$_2$ | −0.267 (2) | 0.016 (1) | −0.243 (1) | 4.0 (5) |
| C$_3$ | −0.352 (2) | 0.057 (1) | −0.277 (1) | 5.4 (5) |
| C$_4$ | −0.351 (2) | 0.122 (1) | −0.233 (2) | 5.9 (6) |
| C$_5$ | −0.264 (2) | 0.150 (1) | −0.167 (1) | 5.4 (6) |
| C$_6$ | −0.169 (2) | 0.111 (1) | −0.134 (1) | 3.5 (4) |
| C$_7$ | 0.306 (2) | 0.081 (1) | 0.082 (1) | 4.8 (5) |
| C$_8$ | 0.409 (2) | 0.104 (1) | 0.151 (1) | 4.4 (5) |
| C$_9$ | 0.495 (2) | 0.067 (1) | 0.170 (1) | 5.4 (6) |
| C$_{10}$ | 0.486 (2) | 0.003 (1) | 0.122 (2) | 5.6 (6) |
| C$_{11}$ | 0.386 (2) | −0.023 (1) | 0.055 (2) | 5.6 (6) |
| C$_{12}$ | 0.302 (2) | 0.016 (1) | 0.037 (1) | 4.9 (5) |
| Bu$_1$C$_1$ | 0.171 (2) | 0.299 (1) | 0.326 (1) | 5.1 (5) |
| Bu$_1$C$_2$ | 0.265 (3) | 0.251 (2) | 0.349 (2) | 7.3 (9) |
| Bu$_1$C$_3$ | 0.356 (2) | 0.276 (1) | 0.449 (2) | 7.7 (7) |
| Bu$_1$C$_4$ | 0.456 (2) | 0.231 (1) | 0.467 (1) | 7.4 (6) |
| Bu$_2$C$_1$ | 0.114 (2) | 0.287 (1) | 0.144 (2) | 7.3 (7) |
| Bu$_2$C$_2$ | 0.155 (2) | 0.361 (1) | 0.138 (1) | 6.9 (5) |
| Bu$_2$C$_3$ | 0.210 (3) | 0.354 (2) | 0.065 (2) | 8.8 (9) |
| Bu$_2$C$_4$ | 0.237 (2) | 0.424 (1) | 0.049 (2) | 8.5 (6) |
| Bu$_3$C$_1$ | −0.003 (3) | 0.341 (1) | 0.211 (2) | 7.4 (7) |
| Bu$_3$C$_2$ | −0.116 (2) | 0.327 (1) | 0.111 (2) | 7.7 (7) |
| Bu$_3$C$_3$ | −0.185 (3) | 0.390 (1) | 0.109 (2) | 7.7 (8) |
| Bu$_3$C$_4$ | −0.288 (3) | 0.379 (2) | 0.018 (2) | 11.1 (9) |
| Bu$_4$C$_1$ | 0.038 (2) | 0.205 (1) | 0.219 (2) | 6.3 (7) |
| Bu$_4$C$_2$ | −0.010 (2) | 0.192 (1) | 0.293 (2) | 7.2 (6) |
| Bu$_4$C$_3$ | −0.049 (3) | 0.116 (2) | 0.277 (2) | 8.9 (9) |
| Bu$_4$C$_4$ | −0.094 (3) | 0.091 (1) | 0.354 (2) | 9.1 (8) |
| BuN | 0.072 (2) | 0.282 (1) | 0.225 (1) | 5.0 (4) |

| Final Anisotropic Thermal Parameters | | | | | | |
|---|---|---|---|---|---|---|
| Atom | $\beta_{11}$[c] | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
| Co | 0.0077 (3) | 0.0030 (1) | 0.0052 (2) | −0.0002 (1) | 0.0035 (2) | 0.0001 (1) |
| S$_1$ | 0.0097 (8) | 0.0032 (2) | 0.0072 (4) | −0.0009 (3) | 0.0049 (4) | 0.0000 (2) |
| S$_2$ | 0.0087 (7) | 0.0038 (2) | 0.0062 (4) | −0.0005 (3) | 0.0042 (4) | −0.0009 (2) |
| S$_3$ | 0.0060 (6) | 0.0025 (2) | 0.0052 (3) | 0.0003 (3) | 0.0033 (4) | −0.0002 (2) |
| S$_4$ | 0.0096 (7) | 0.0028 (2) | 0.0066 (4) | −0.0007 (3) | 0.0042 (4) | −0.0003 (2) |
| Cl$_1$ | 0.0103 (7) | 0.0032 (2) | 0.0066 (4) | 0.0000 (3) | 0.0035 (4) | −0.0006 (3) |
| Cl$_2$ | 0.0077 (8) | 0.0065 (3) | 0.0081 (4) | 0.0005 (4) | 0.0020 (4) | 0.0004 (3) |
| Cl$_3$ | 0.0116 (10) | 0.0067 (3) | 0.0115 (6) | 0.0048 (4) | 0.0025 (6) | 0.0004 (4) |
| Cl$_4$ | 0.0145 (9) | 0.0037 (2) | 0.0108 (5) | 0.0020 (4) | 0.0049 (5) | −0.0006 (3) |
| Cl$_5$ | 0.0122 (9) | 0.0050 (3) | 0.0098 (5) | −0.0031 (4) | 0.0050 (5) | −0.0018 (3) |
| Cl$_6$ | 0.0074 (8) | 0.0094 (4) | 0.0097 (5) | −0.0021 (4) | 0.0030 (5) | −0.0007 (4) |
| Cl$_7$ | 0.0084 (8) | 0.0080 (4) | 0.0107 (5) | 0.0019 (4) | 0.0041 (5) | 0.0003 (4) |
| Cl$_8$ | 0.0109 (8) | 0.0057 (3) | 0.0102 (5) | 0.0016 (4) | 0.0059 (5) | −0.0012 (3) |

[a] The estimated standard deviation in the least significant figure is given in parentheses. [b] From the isotropic refinement. [c] The general form for the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{23}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Because of the statistical method used for scaling the data and the refinement of individual level scale factors, the $\beta_{11}$'s are on an arbitrary scale. However, an examination of the final difference Fourier map based on the isotropic refinement clearly shows anisotropic vibration by the heavy atoms and a rocking motion of the dimer in the solid.

independent anion unit were refined while the cation parameters were held fixed. Next, all positional, scale, and isotropic thermal parameters were refined while the anisotropic thermal parameters were held fixed. Finally, a cycle was repeated in which the positional and thermal parameters of the anion unit were refined. This partial anisotropic refinement for 1588 nonzero reflections converged to conventional and weighted *R* factors of 0.094 and 0.080, respectively. The highest peak on the final difference Fourier based on this refinement is 0.47 e/Å$^3$ which is about 20% of the height of a carbon atom in this structure. Reasonable positions for 30 of the 36 hydrogen atoms of the cation were determined from this final difference Fourier. The contributions of these hydrogen atoms to $|F_c|$ were not included in any further calculations.

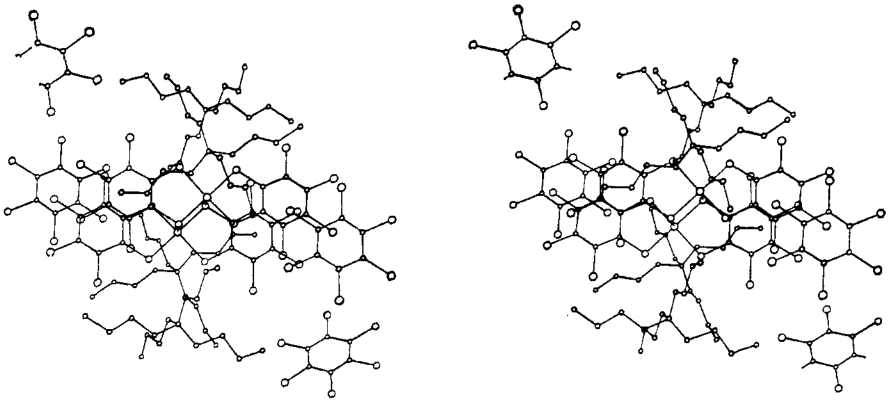

Figure 1. Stereoscopic view of the packing of $[n\text{-}(C_4H_9)_4N]_2[Co_2(S_2C_6Cl_4)_4]$ in the crystal. These drawings constitute a stereo pair and may be viewed with a hand viewer.

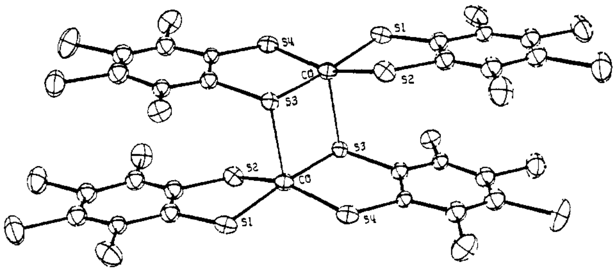

Figure 2. A perspective drawing of the $[Co_2(S_2C_6Cl_4)_4]^{2-}$ dimer unit showing the dimer linkages between the planar $Co(S_2C_6Cl_4)_2^-$ units. The thermal ellipsoids have been scaled to 30% probability distributions.

The parameters obtained in this final refinement are taken as the final parameters for the structure and are given in Table I. Standard deviations of the parameters, as obtained from the appropriate inverse matrix, are also given.[12] Despite a weighted $R$ factor of 0.080, the weighting scheme yielded a value of 4.51 for the standard deviation of an observation of unit weight. The scheme tended to greatly weigh down very strong reflections at low values of $2\theta$ and very weak ones at higher angles. A more preferable scheme might have been based on $I$ and $F_o$ values instead of $I^2$ alone.

**Description of the Structure.** The structure described by the unit cell constants, the symmetry operations of the space group, and the atomic parameters of Table I consists of the packing of discrete $[Co_2(S_2C_6Cl_4)_4]^{2-}$ dimeric units and essentially tetrahedral $(n\text{-}C_4H_9)_4N^+$ cations. Figure 1 is a stereoscopic view of the packing of $[(n\text{-}C_4H_9)_4N]_2[Co_2(S_2C_6Cl_4)_4]$ molecules in the crystal. The anionic dimers are required to be centrosymmetric with the center of symmetry at the origin located half-way between the two cobalt atoms. In the dimer, two nearly planar $[Co(S_2C_6Cl_4)_2]^-$ units lie parallel to one another such that the Co atom of each planar unit is directly opposite a sulfur atom belonging to the second such unit. Dimerization occurs through the formation of two Co–S bonds of length 2.404 Å. The Co···Co distance in the dimer is 3.099 Å. In Figure 2, the $[Co_2(S_2C_6Cl_4)_4]^{2-}$ dimeric unit is shown in perspective. The dimer structure which we observe here for $[Co_2(S_2C_6Cl_4)_2]^{2-}$ is quite similar to that found by Enemark and Lipscomb for the neutral complex $[Co_2(S_2C_2(CF_3)_2)_4]$.[7] This type of dimeric structure has also been observed in several complexes of Cu(II) including the neutral bis complex with N,N-dipropyldithiocarbamate.[13a] In addition, the very recent X-ray study of the closely related anionic complex $[Fe_2(S_2C_2(CN)_2)_4]^{2-}$ reveals essentially the same dimeric structure.[13b]

The coordination about the Co atom is best described as square pyramidal with the metal displaced 0.26 Å out of the plane of the four basal S atoms toward the apical S atom of the second planar unit. The average Co–S distance in the base of the pyramid is 2.185 Å, and the apical Co–S distance is 2.404 Å with estimated standard deviations for these distances of 0.007 Å. These distances compare favorably with those found for the $[Co_2(S_2C_2(CF_3)_2)_4]$ dimer in which the average basal Co–S distance is 2.161 Å and the apical Co–S distance is 2.382 Å. However, the Co···Co distance of 3.10 Å in $[Co_2(S_2C_6Cl_4)_4]^{2-}$ is much longer than the corresponding value of 2.78 Å found in the $[Co_2(S_2C_2(CF_3)_2)_4]$ dimer. The longer Co···Co distance reflects the fact that the atoms in the $[Co_2(S_2C_6Cl_4)_4]^{2-}$ dimer are less removed from the plane of the basal S atoms than in the neutral $[Co_2(S_2C_2(CF_3)_2)_4]$ complex where it is observed that the Co atoms are displaced 0.37 Å out of the corresponding planes. A comparison of the apical Co–S bond distances with the sum of the Co–S single bond radii (2.20 Å)[14] indicates that the bonding between the planar units in both dimer structures is somewhat weaker than that of a Co–S single bond. In addition, the sum of single bond radii for a hypothetical Co–Co bond (2.32 Å)[14] suggests that any interactions between the Co atoms in the $[Co_2(S_2C_2Cl_4)_4]^{2-}$ dimer are very weak and are probably negligible compared to the Co–S bonding interactions.

The molecular dimensions[15] for the complex are

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[12] A compilation of observed and calculated structure amplitudes has been deposited as Document No. 9881 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. Copies may be secured by citing the document number and remitting in advance $1.25 for photoprints or $1.25 for 35-mm microfilm, payable to Chief, Photoduplication Service, Library of Congress.

[13] (a) A. Pignedoli and G. Peyronel, *Gazz. Chim. Ital.*, **92**, 745 (1962); (b) I. Bernal and W. C. Hamilton, *Inorg. Chem.*, **6**, 2003 (1967).

[14] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 255, 256.

[15] The molecular dimensions were obtained by the use of the following programs: "SADIAN—Search for Atomic Distances and Angles," a local modification of the corresponding program from Brookhaven National Laboratory, and "MGEOM—Molecular Ge-

tabulated in Tables II and III, and the structure and numbering system of the half-dimer unit $[Co(S_2C_6Cl_4)_2]^-$ is shown in Figure 3. The $[Co(S_2C_6Cl_4)_2]^-$ unit is only approximately planar. The best weighted least-squares plane through the four S atoms is given by the equation

$$-0.383 \times 0.414y + 0.826z = -1.391$$

in orthonormal coordinates.[16] Deviations of the Co and S atoms from this plane are given in Table IV. The S atoms have a very slightly puckered geometry with $S_1$ and $S_3$ above the plane and $S_2$ and $S_4$ below it.

**Table II.** Principal Intramolecular Bond Distances in the $[Co_2(S_2C_6Cl_4)_4]^{2-}$ Dimer

| Atoms | Distance, Å | Atoms | Distance, Å |
|---|---|---|---|
| Co–Co′ | 3.099 (4)[a] | $C_6$–$C_1$ | 1.41 (3) |
| Co–$S_3$′ | 2.404 (7) | $C_7$–$C_8$ | 1.44 (3) |
| Co–$S_1$ | 2.183 (7) | $C_8$–$C_9$ | 1.32 (4) |
| Co–$S_2$ | 2.169 (7) | $C_9C_{10}$ | 1.40 (3) |
| Co–$S_3$ | 2.184 (6) | $C_{10}$–$C_{11}$ | 1.43 (4) |
| Co–$S_4$ | 2.205 (7) | $C_{11}$–$C_{12}$ | 1.31 (4) |
| $S_1$–$C_7$ | 1.72 (2) | $C_{12}$–$C_7$ | 1.41 (3) |
| $S_2$–$C_{12}$ | 1.78 (2) | $C_2$–$Cl_1$ | 1.70 (2) |
| $S_3$–$C_1$ | 1.78 (2) | $C_3$–$Cl_2$ | 1.75 (3) |
| $S_4$–$C_6$ | 1.75 (2) | $C_4$–$Cl_3$ | 1.73 (3) |
| $C_1$–$C_2$ | 1.39 (3) | $C_5$–$Cl_4$ | 1.71 (2) |
| $C_2$–$C_3$ | 1.32 (3) | $C_8$–$Cl_5$ | 1.71 (2) |
| $C_3$–$C_4$ | 1.40 (3) | $C_9$–$Cl_6$ | 1.69 (3) |
| $C_4$–$C_5$ | 1.32 (4) | $C_{10}$–$Cl_7$ | 1.74 (3) |
| $C_5$–$C_6$ | 1.41 (3) | $C_{11}$–$Cl_8$ | 1.70 (2) |
| | Mean Bond Distances | | |
| Co–S (basal) | 2.185 | C–C | 1.38 |
| S–C | 1.76 | C–Cl | 1.72 |

[a] Estimated standard deviations are given in parentheses.

**Table III.** Principal Intramolecular Bond Angles in the $[Co_2(S_2C_6Cl_4)_4]^{2-}$ Dimer

| Atoms | Angle, deg | Atoms | Angle, deg |
|---|---|---|---|
| $S_1$–Co–$S_2$ | 90.5 (2)[a] | $Cl_8$–$C_{11}$–$C_{10}$ | 119.6 (1.8) |
| $S_2$–Co–$S_3$ | 86.9 (2) | $Cl_8$–$C_{11}$–$C_{12}$ | 122.5 (1.8) |
| $S_3$–Co–$S_4$ | 90.8 (2) | $C_{10}$–$C_{11}$–$C_{12}$ | 117.8 (2.2) |
| $S_4$–Co–$S_1$ | 89.3 (2) | $S_2$–$C_{12}$–$C_{11}$ | 120.4 (1.8) |
| $S_3$′–Co–$S_2$ | 91.6 (2) | $S_2$–$C_{12}$–$C_7$ | 116.3 (1.9) |
| $S_3$′–Co–$S_2$ | 104.1 (2) | $C_{11}$–$C_{12}$–$C_7$ | 123.4 (1.9) |
| $S_3$′–Co–$S_3$ | 95.2 (2) | $S_3$–$C_1$–$C_6$ | 117.5 (1.5) |
| $S_3$′–Co–$S_4$ | 97.0 (2) | $S_3$–$C_1$–$C_2$ | 119.7 (1.5) |
| Co–$S_1$–$C_7$ | 104.1 (7) | $C_6$–$C_1$–$C_2$ | 122.8 (1.9) |
| Co–$S_2$–$C_{12}$ | 104.5 (7) | $Cl_1$–$C_2$–$C_1$ | 120.3 (1.9) |
| Co–$S_3$–$C_1$ | 105.7 (6) | $Cl_1$–$C_2$–$C_3$ | 121.3 (2.0) |
| Co-$S_4$-$C_6$ | 105.1 (7) | $C_1$–$C_2$–$C_3$ | 117.8 (2.0) |
| $S_1$–$C_7$–$C_{12}$ | 121.2 (1.6) | $Cl_2$–$C_3$–$C_2$ | 119.4 (2.0) |
| $S_1$–$C_7$–$C_8$ | 122.2 (1.6) | $Cl_2$–$C_3$–$C_4$ | 120.2 (1.9) |
| $C_8$–$C_7$–$C_{12}$ | 116.5 (2.2) | $C_2$–$C_3$–$C_4$ | 120.0 (2.3) |
| $Cl_5$–$C_8$–$C_7$ | 117.2 (1.9) | $Cl_3$–$C_4$–$C_3$ | 118.2 (1.9) |
| $Cl_5$–$C_8$–$C_9$ | 120.8 (1.9) | $Cl_3$–$C_4$–$C_5$ | 118.6 (1.8) |
| $C_7$–$C_8$–$C_9$ | 122.0 (2.0) | $C_3$–$C_4$–$C_5$ | 123.1 (2.2) |
| $Cl_6$–$C_9$–$C_8$ | 121.9 (2.0) | $Cl_4$–$C_5$–$C_4$ | 124.0 (2.2) |
| $Cl_6$–$C_9$–$C_{10}$ | 119.5 (1.7) | $Cl_4$–$C_5$-$C_6$ | 116.6 (1.6) |
| $C_8$–$C_9$–$C_{10}$ | 118.6 (1.9) | $C_4$–$C_5$–$C_6$ | 119.4 (2.2) |
| $Cl_7$–$C_{10}$–$C_9$ | 119.3 (1.7) | $S_4$–$C_6$–$C_5$ | 123.2 (1.5) |
| $Cl_7$–$C_{10}$–$C_{11}$ | 119.0 (1.7) | $S_4$–$C_6$–$C_1$ | 120.6 (1.5) |
| $C_9$–$C_{10}$–$C_{11}$ | 121.7 (1.9) | $C_5$–$C_6$–$C_1$ | 116.0 (1.6) |
| | Mean Bond Angles | | |
| S–Co–S (ring) | 90.7 | C–C–C | 118.3 |
| Co–S–C | 104.6 | Cl–C–C | 119.5 |
| S–C–C | 118.9 | | |

[a] Estimated standard deviations are given in parentheses.

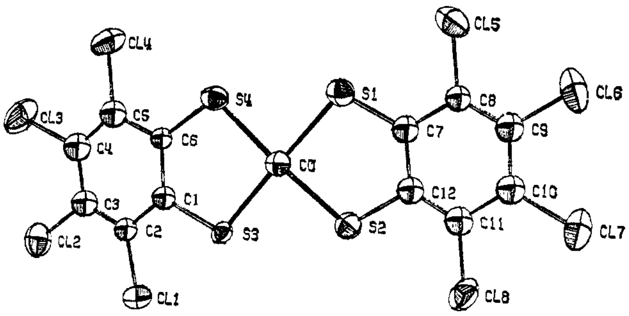

Figure 3. A drawing of the planar $Co(S_2C_6Cl_4)_2^-$ unit showing the numbering system employed. The thermal ellipsoids have been scaled to 30% probability distributions.

**Table IV.** Distances (Å) of the Co and S Atoms from the Best Plane through $S_1$, $S_2$, $S_3$, and $S_4$

| Atom | Distance from plane |
|---|---|
| Co | +0.26 |
| $S_1$ | +0.15 |
| $S_2$ | −0.14 |
| $S_3$ | +0.12 |
| $S_4$ | −0.13 |

The anion benzene rings are reasonably planar. The ring consisting of $C_7$–$C_{12}$ does not deviate significantly from planarity. The largest deviation of the Cl atoms from the plane through this ring is $Cl_5$ at 0.07 Å. In contrast, the other benzene ring consisting of $C_1$–$C_6$ is only planar within ±0.06 Å. The best weighted least-squares plane through the entire $[Co(S_2C_6Cl_4)_2]^-$ unit is given by the equation

$$-0.503x - 0.444y + 0.742z = 1.683$$
$$\text{(orthonormal coordinates)}$$

The rather approximate planarity of the half-dimer unit can be seen in Figure 2. The deviations of all the atoms from this plane are given in Table V. The deviations of the atoms $Cl_1$–$Cl_4$ must be interpreted as a result of nonbonded repulsion forces in the dimer unit. However, these deviations from planarity do not appear to be as great as those found in the $[Co_2(S_2C_2(CF_3)_2)_4]$ dimer, presumably because of the presence of the bulky $CF_3$ groups in the latter complex. The deviations of the Co and $S_3$ atoms from the weighted least-squares plane through the monomeric unit are in the direction of the symmetry related atoms $S_3$′ and Co′, respectively. The large deviations of these atoms from the plane are probably caused by the attractive forces responsible for the formation of the two Co–S bonds which result in the dimerization.

**The Tetra-*n*-butylammonium Ion.** The tetra-*n*-butylammonium ion has its expected tetrahedral shape. The important dimensions of this ion are listed in Table VI. All the butyl chains adopt the *trans* configuration.

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ometry Program for IBM 7094," written by J. S. Wood, Massachusetts Institute of Technology, 1964.

(16) The orthogonal $y$ axis is taken to be coincident with the $b$ axis of the unit cell, the orthogonal $z$ axis is taken in the direction of $a \times b$, and the orthogonal $x$ axis is given by $y \times z$.

Table V. Distances (Å) of the Various Atoms from the Best Plane through the Entire $Co(S_2C_6Cl_4)_2^-$ Unit

| Atom | Distance from plane | Atom | Distance from plane |
|---|---|---|---|
| Co | +0.42 | $C_1$ | +0.24 |
| $S_1$ | +0.03 | $C_2$ | +0.12 |
| $S_2$ | +0.12 | $C_3$ | −0.09 |
| $S_3$ | +0.57 | $C_4$ | −0.05 |
| $S_4$ | +0.18 | $C_5$ | 0.00 |
| $Cl_1$ | +0.03 | $C_6$ | +0.11 |
| $Cl_2$ | −0.23 | $C_7$ | −0.03 |
| $Cl_3$ | −0.17 | $C_8$ | −0.01 |
| $Cl_4$ | −0.08 | $C_9$ | −0.05 |
| $Cl_5$ | +0.10 | $C_{10}$ | −0.10 |
| $Cl_6$ | −0.01 | $C_{11}$ | −0.08 |
| $Cl_7$ | −0.08 | $C_{12}$ | −0.07 |
| $Cl_8$ | −0.14 | | |

The dihedral angles of these chains are listed in Table VII. The angles are small showing that the butyl chains are very nearly planar.

Table VI. Bond Distances and Angles in the Tetra-*n*-butylammonium Ion

| Atoms | Distance, Å | Atoms | Angle, deg |
|---|---|---|---|
| N–$Bu_1C_1$ | 1.62 (3)[a] | $Bu_1C_1$–N–$Bu_2C_1$ | 106 (1) |
| N–$Bu_2C_1$ | 1.58 (3) | $Bu_1C_1$–N–$Bu_3C_1$ | 104 (2) |
| N–$Bu_3$-$C_1$ | 1.49 (3) | $Bu_1C_1$–N–$Bu_4C_1$ | 112 (2) |
| N–$Bu_4C_1$ | 1.53 (3) | $Bu_2C_1$–N–$Bu_3C_1$ | 108 (2) |
| $Bu_1C_1$–$Bu_1C_2$ | 1.51 (4) | $Bu_2C_1$–N–$Bu_4C_1$ | 103 (2) |
| $Bu_1C_2$–$Bu_1C_3$ | 1.60 (4) | $Bu_3C_1$–N–$Bu_4C_1$ | 113 (2) |
| $Bu_1C_3$–$Bu_1C_4$ | 1.55 (4) | N-$Bu_1C_1$–$Bu_1C_2$ | 114 (2) |
| $Bu_2C_1$–$Bu_2C_2$ | 1.52 (3) | $Bu_1C_1$–$Bu_1C_2$–$Bu_1C_3$ | 108 (2) |
| $Bu_2C_2$–$Bu_2C_3$ | 1.61 (4) | $Bu_1C_2$–$Bu_1C_3$–$Bu_1C_4$ | 107 (2) |
| $Bu_2C_3$–$Bu_2C_4$ | 1.44 (4) | N-$Bu_2C_1$–$Bu_2C_2$ | 112 (2) |
| $Bu_3C_1$–$Bu_3C_2$ | 1.70 (4) | $Bu_2C_1$–$Bu_2C_2$–$Bu_2C_3$ | 106 (2) |
| $Bu_3C_2$–$Bu_3C_3$ | 1.52 (4) | $Bu_2C_2$–$Bu_2C_3$–$Bu_2C_4$ | 107 (2) |
| $Bu_3C_3$–$Bu_3C_4$ | 1.54 (5) | N-$Bu_3C_1$-$Bu_3C_2$ | 109 (2) |
| $Bu_4C_1$–$Bu_4C_2$ | 1.56 (4) | $Bu_3C_1$–$Bu_3C_2$–$Bu_3C_3$ | 103 (2) |
| $Bu_4C_2$–$Bu_4C_3$ | 1.52 (4) | $Bu_3C_2$–$Bu_3C_3$–$Bu_3C_4$ | 104 (2) |
| $Bu_4C_3$–$Bu_4C_4$ | 1.63 (4) | N-$Bu_4C_1$–$Bu_4C_2$ | 109 (2) |
| | | $Bu_4C_1$–$Bu_4C_2$–$Bu_4C_3$ | 105 (2) |
| | | $Bu_4C_2$–$Bu_4C_3$–$Bu_4C_4$ | 112 (2) |
| Mean N–C distance | 1.55 Å | Mean C–N–C angle | 109.2° |
| Mean C–C distance | 1.56 Å | Mean C(N)–C–C angle | 108.2° |

[a] Estimated standard deviations are given in parentheses.

Table VII. Dihedral Angles in the Four Butyl Chains of the Tetra-*n*-butylammonium Ion

| Plane (1) defined by atoms | Plane (2) defined by atoms | Dihedral angle, deg |
|---|---|---|
| $Bu_1C_1$–$Bu_1C_2$–$Bu_1C_3$ | $Bu_1C_2$–$Bu_1C_3$–$Bu_1C_4$ | 5.7 |
| $Bu_2C_1$–$Bu_2C_2$–$Bu_2C_3$ | $Bu_2C_2$–$Bu_2C_3$–$Bu_2C_4$ | 7.3 |
| $Bu_3C_1$–$Bu_3C_2$–$Bu_3C_3$ | $Bu_3C_2$–$Bu_3C_3$–$Bu_3C_4$ | 0.9 |
| $Bu_4C_1$–$Bu_4C_2$–$Bu_4C_3$ | $Bu_4C_2$–$Bu_4C_3$–$Bu_4C_4$ | 4.2 |
| Butyl-1–N–Butyl-3 | Butyl-2–N–Butyl-4 | 87.2 |

The four C–N bonds have an average length of 1.55 ± 0.04 Å. The six bond angles about the nitrogen atom (C–N–C) average 109.2° which is well within experimental error of the tetrahedral angle. However, several of the individual bond angles do show some significant deviations from this value. In the butyl chain, the mean C–C distance is 1.56 ± 0.05 Å. The mean value of the 12 N–C–C and C–C–C angles is 108.2°, close to the tetrahedral angle. It should be noted that the block diagonal refinement, which we employed, produces underestimates of positional and thermal parameter errors. The estimated standard deviations for the cation distances and angles should be multiplied by approximately two in order to make them more consistent with the observed agreement. In addition, estimated standard deviations do not represent absolute error ranges.

The closest approach of the cation atoms (except for the hydrogens) to the dimer anion is 3.44 Å and to the Co atom is 4.23 Å.

## Discussion

It is relevant to compare the $[Co_2(S_2C_6Cl_4)_4]^{2-}$ structure with other known structures of Co complexes containing similar sulfur ligands. Besides the neutral $[Co_2(S_2C_2(CF_3)_2)_4]$ species, structures are also available for the related monanion $[Co(tdt)_2]^-$ [8] and the dianion $[Co(S_2C_2(CN)_2)_2]^{2-}$.[17] The important molecular dimensions of each are summarized in Table VIII. Amazingly, despite the differences in oxidation states and the fact that two of these complexes are dimeric, there are only slightly significant differences in the dimensions of the $(CoS_2C_2)$ chelate rings. The greatest difference in the chelate rings occurs in the S–C bond distances which are shorter in the complexes of the substituted ethylene ligands than in the complexes containing substituted benzene ligands. In both of the monomeric complexes, the Co atom is located at a center of symmetry and the anions are essentially planar. In contrast, in both dimeric complexes, the Co atom is displaced out of the plane of the four sulfur atoms and the deviations from planarity are significant. Since the molecular dimensions of the Co–S–C framework of the two complexes containing substituted benzene ligands, $[Co_2(S_2C_6Cl_4)_4]^{2-}$ and $[Co(tdt)_2]^-$, are virtually identical, it is evident that electronic effects are not manifested in differences in bond lengths.

From steric considerations, the substituents in both dimeric complexes should oppose dimerization. The bulky size of the Cl and $CF_3$ groups should favor a structure with the two planar units widely separated. Yet these electron-withdrawing substituents must remove sufficient electron density from the vicinity of the Co atom such that dimerization through S→Co bonding becomes favorable. *The electronic nature of the substituent thus appears to control the extent of dimerization.*

In an attempt to probe deeper into the electronic structural factors associated with dimerization, we make use of results of molecular orbital calculations of the SCCC type performed on the $Ni(bdt)_2^-$ and $Ni(S_2C_6Cl_4)_2^-$ model systems. The spin-doublet $NiL_2^-$ complexes were chosen as models because detailed polarographic, electronic spectral, and esr data are available for comparison purposes. The calculations assume no initial hybridization of the sulfur 3s and 3p orbitals and are consistent with the polarographic,[3] electronic spectra,[9] and esr data[18] for the $NiL_2^-$ complexes.

A comparison of the electronic structures of these two model systems reveals a possible reason for the

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(17) J. D. Forrester, A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, 3, 1500 (1964).

(18) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).

**Table VIII.** Comparison of Dimensions of Some Co Complexes

| | $[Co_2(S_2C_6Cl_4)_4]^{2-}$ | $[Co_2(S_2C_2(CF_3)_2)_4]$ | $[Co(tdt)_2]^-$ | $[Co(S_2C_2(CN)_2)_2]^{2-}$ |
|---|---|---|---|---|
| Bond distances, Å | | | | |
| Co–S | 2.18 | 2.16 | 2.17 | 2.16 |
| Co–S′ | 2.40 | 2.38 | ... | ... |
| Co–Co′ | 3.10 | 2.78 | 10.21 | 9.81 |
| S–C | 1.76 | 1.69 | 1.77 | 1.72 |
| C–C | 1.38 | 1.39 | 1.40 | 1.34 |
| Bond angles, deg | | | | |
| S–Co–S (intra) | 90.7 | 89.8 | 91.3 | 91.4 |
| S–Co–S (inter) | 88.1 | 86.4 | 88.7 | 88.6 |
| Co–S–C | 104.8 | 105.5 | 105.3 | 103.8 |

dimerization of the $Co(S_2C_6Cl_4)_2^-$ complex. The MO calculation performed on the $Ni(bdt)_2^-$ complex indicates the metal $4p_z$ orbital is a substantial participant in the out-of-plane $\pi$ system. Specifically, the calculation gives 12% $4p_z$ character to the highest filled $b_{1u}$ molecular orbital. Experimental evidence of the strong involvement of $4p_z$ in $\pi$ bonding is the absence of solvent perturbations on the electronic spectrum of $Ni(bdt)_2^-$; it also shows no tendency to react with itself to give a dimer or with other electron donors to give "adduct" complexes. In contrast, the MO calculation performed on the $Ni(S_2C_6Cl_4)_2^-$ model system clearly shows a smaller involvement (8%) of the $4p_z$ orbital in the $b_{1u}$ $\pi$ system. In simple terms, electron density in the $b_{1u}\pi$ molecular orbital is drawn away from $4p_z$ into the aromatic ring by the electron-withdrawing chloro substituents. As a result, the $Ni(S_2C_6Cl_4)_2^-$ complex experiences axial perturbations in strongly coordinating solvents. Thus, the availability of the metal $4p_z$ orbital for $\sigma$ bonding to the solvent is a factor in determining which complexes undergo axial interactions in solution.

The electron-withdrawing chloro substituents affect electron density in the other metal orbitals, especially those conjugated with the ligand $\pi$ system. The electron-deficient nature of the central metal atoms is a measure of electron withdrawal from all of these orbitals. Thus, in $Co(S_2C_6Cl_4)_2^-$, the general electron-deficient nature of the Co atom, along with the specific availability of the $4p_z$ orbital, is suggested as the explanation of dimerization. In complexes such as $Co(tdt)_2^-$, the metal orbitals, especially the $4p_z$ orbital, must have such a large share of the occupied orbitals that dimerization is unfavorable.

A model of the bonding in the dimer can be constructed by using the two $4p_z$ orbitals from the two electron-deficient Co atoms as acceptors, and for each of the two donors the highest occupied, out-of-plane $\pi$ orbital which has a large component of sulfur $3p_z$. In this model each Co atom in a $Co(S_2C_6Cl_4)_2^-$ unit forms a $\sigma$ bond with the filled "sulfur" $\pi$ orbital on the other $Co(S_2C_6Cl_4)_2^-$ unit, making each Co atom five-coordinate. The two Co–S $\sigma$ bonds that bind the dimer must be rather weak, because even in relatively noncoordinating solvents (cyclohexane and tetrahydrofuran) the dimer dissociates to give two $Co(S_2C_6Cl_4)_2^-$ monomers. The long bond length obtained for the Co–S apical bond from the X-ray structure determination is further evidence of the weakness of this bond.

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