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Semiquinone Radical Anion Coordination to Divalent Cobalt and Nickel. Structural Features of the Bis(3,5-di-*tert*-butyl-1,2-semiquinone)cobalt(II) Tetramer

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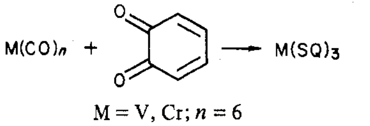
The complex $Co(O_2C_6H_2(t\text{-}Bu)_2)_2$ has been prepared by treating $Co_2(CO)_8$ with 3,5-di-*tert*-butyl-1,2-benzoquinone in benzene solution. The dark green complex has been shown by a crystallographic molecular structure determination to be tetrameric, $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8$, with octahedrally coordinated metal ions. Crystals form as benzene solvates in the triclinic space group $P\bar{1}$ with one independent centrosymmetric complex molecule per unit cell. Unit cell dimensions are $a = 15.594$ (5) Å, $b = 15.902$ (7) Å, $c = 15.972$ (5) Å, $\alpha = 94.34$ (2)°, $\beta = 107.92$ (3)°, $\gamma = 118.48$ (3)°, and $V = 3193.1$ Å^3. Cobalt–oxygen bond lengths within the coordination sphere are typical for high-spin Co(II) and carbon–oxygen lengths of the ligands are of the value found for complexed semiquinone ligands. The related nickel complex $Ni_4(O_2C_6H_2(t\text{-}Bu)_2)_8$ is isostructural with the cobalt analogue. Spectral similarities between complexes of Ni and Co prepared with tetrachloro-1,2-benzoquinone, 9,10-phenanthrenequinone, and 3,5-di-*tert*-butyl-1,2-benzoquinone with related tris(semiquinone) complexes of V, Fe, and Cr indicate that these should be formulated as bis(semiquinone) complexes of the divalent metal ions likely having oligomeric structures with octahedrally coordinated metal ions. The room-temperature magnetic susceptibilities of these compounds are discussed in terms of an antiferromagnetic metal–ligand exchange interaction similar to that found for the tris complexes.

Introduction

Magnetic exchange between paramagnetic metal ions linked by one or more ligand bridges has been a subject of interest for many years. In cases where exchange is relatively weak, the interaction can be measured in terms of a change in magnetic moment as a function of temperature. Magnetic exchange between a paramagnetic organic radical ligand and the unpaired electrons of a complexed metal ion that can be measured by using conventional spectroscopic and magnetic methods occurs only in a few rare systems. Nitroxyl radicals have been used as spin labels for biological molecules containing paramagnetic metal ions.[1] Electron paramagnetic resonance is generally used to investigate metal–nitroxyl coupling in systems of this type and in simpler complexes prepared with nitroxyl ligands.[2] A number of complexes containing bipyridyl radical anion ligands seem to exhibit temperature-dependent paramagnetism resulting from metal–ligand exchange.[3] The Fe–O_2 interaction in oxygenated heme has been viewed as involving antiferromagnetic coupling between triplet O_2 and a triplet Fe^{2+} ion[4] and the results of a recent variable-temperature magnetic susceptibility measurement were interpreted to indicate the thermal population of a triplet excited state.[5]

The occurrence of paramagnetic ligands complexed to a paramagnetic metal center requires that the ground-state levels of ligand and metal be on the same order of energy. Otherwise formal electron transfer will occur with ligand oxidation or reduction. It also requires minimal metal–ligand delocalization which would promote spin coupling in the array of resulting molecular orbital levels. The neutral 1,2-dithiolene complexes clearly illustrate this behavior.[6] In the course of investigating tris complexes prepared by treating a first-row metal carbonyl with a neutral *o*-quinone (eq 1), we found from the physical,



(1)

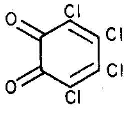
$M = V, Cr; n = 6$
$M = Fe; n = 5$

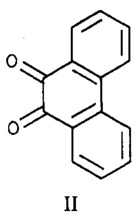
spectral, and magnetic properties of the resulting compounds that they were best formulated as tris(semiquinone) complexes of trivalent metal ions.[7,8] Further work with metals of the second and third transition series has shown that, due to a disparity between ligand π^* and filled metal electronic levels, these are clearly tris(catecholato) complexes of hexavalent metals.[9,10] In the interest of extending our investigation of the first-row metal–semiquinone complexes, we now report the results of studies carried out on complexes prepared with cobalt and nickel. Ligands used in this investigation include tetrachloro-1,2-benzoquinone (I), 9,10-phenanthrenequinone (II), and 3,5-di-*tert*-butyl-1,2-benzoquinone (III).

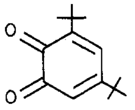
Table I. Crystallographic Data for $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8 \cdot 2C_6H_6$

fw: 2154.2
triclinic
space group $P\bar{1}$
$a = 15.594$ (5) Å
$b = 15.902$ (7) Å
$c = 15.972$ (5) Å
$\alpha = 94.34$ (2)°
$\beta = 107.92$ (3)°
$\gamma = 118.48$ (3)°
$V = 3193.1$ Å^3

$d(\text{calcd}) = 1.124$ g cm^{-3}
$d(\text{exptl}) = 1.119$ g cm^{-3}
$Z = 1$
$\mu = 5.91$ cm^{-1}
Mo Kα radiation
scan rate: 4°/min
2θ limits: $3° \leqslant 45°$
scan range: ±0.7°
data collected: 8343
data $F_o^2 > 3\sigma(F_o^2)$: 4828
$p = 0.04$


I


II


III

Experimental Section

Compound Synthesis. The preparations of $Ni(O_2C_6Cl_4)_2$ and $Ni(O_2C_6H_2(t\text{-}Bu)_2)_2$ have been reported previously by Holm and coworkers.[11] Complexes of 9,10-phenanthrenequinone were prepared by using the procedure of Calderazzo[12] but with toluene as the solvent for the reaction.

$Co(O_2C_6H_2(t\text{-}Bu)_2)_2$. Dicobalt octacarbonyl (0.68 g, 2 mmol) was dissolved in 25 mL of benzene. Over the period of 10 min, 1.76 g (8 mmol) of 3,5-di-*tert*-butyl-1,2-benzoquinone dissolved in 25 mL of benzene was added under a N_2 atmosphere. The reaction mixture gradually turned dark green with large prismatic crystals of $[Co(O_2C_6H_2(t\text{-}Bu)_2)_2]_4 \cdot 2C_6H_6$ separating from solution over a period of several hours. Total yield of complex obtained was 1.78 g or 73%.

Structure Determination of $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8 \cdot 2C_6H_6$. Preliminary photographs taken on crystals of $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8$ indicated triclinic symmetry. A crystal of dimensions 0.21 × 0.26 × 0.43 mm was mounted and centered on a Syntex P$\bar{1}$ automated diffractometer equipped with a graphite-crystal monochromator. The settings of 15 reflections were used to calculate the cell constants given in Table I. Data were collected by the θ–2θ scan technique with four standard reflections measured periodically throughout data collection. They showed only normal variations in intensity. The locations of the two

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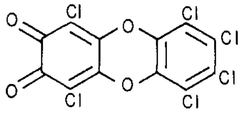
independent cobalt atoms were determined from a Patterson map and standard heavy-atom procedures were used to solve the structure. Sources of scattering factor tables, computer programs, and calculational procedures have been noted.[13] Final cycles of refinement converged with $R_F = 0.065$ and $R_{wF} = 0.074$ for 4828 reflections with $F_o^2 > 3\sigma(F_o^2)$. The final value for the standard deviation of an observation of unit weight was 1.97. Final positional and thermal parameters for $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8 \cdot 2C_6H_6$ are listed in Table II. Values of $10|F_o|$ and $10|F_c|$ (in electrons) are available as supplementary material.

Discussion

Bis(semiquinone) Complexes of Co(II) and Ni(II). Neutral nickel complexes of form $Ni(quinone)_2$ were first reported by Holm and co-workers in 1966.[11] These compounds were prepared in one of two ways, either by direct reaction of $Ni(CO)_4$ with *o*-quinone or by treating Ni^{2+} with catecholate and oxidizing the anionic complex to the neutral form. This work was carried out as an extension of their interest in the 1,2-dithiolene systems, although it was apparent from the properties of the neutral nickel compounds that they were considerably different from their dithiolene analogues and also different from related bis(*p*-quinone)nickel(0) complexes.[14] More recently others have taken advantage of the synthetic procedures outlined in this report to prepare related compounds. Calderazzo has prepared neutral 9,10-phenanthrenequinone complexes of Ni, Co, and Fe by the metal carbonyl–*o*-quinone route.[12] Razuvaev has reported preparing complexes with a wide variety of metals by treating di- and trivalent metal ions with stoichiometric quantities of semiquinone.[15] We have used the metal carbonyl–*o*-quinone procedure previously to prepare complexes of V, Cr, Fe,[7,8] and Mo[9,16] and in this report to prepare bis(3,5-di-*tert*-butyl-1,2-semiquinone)cobalt(II). Attempts to prepare the bis(tetrachloro-1,2-semiquinone)cobalt(II) complex by this procedure have failed. In benzene solution the reaction between $Co_2(CO)_8$ and tetrachloro-1,2-benzoquinone yields an orange-red organic material and the metal chloride $CoCl_2$. Similar products are obtained by simply treating the quinone with magnesium. The organic material seems to be hexachloro-2,3-oxanthrenequinone (IV), which was first reported as the product of the reaction between tetrachlorocatechol and tetrachloro-1,2-benzoquinone[17] and was rediscovered quite recently as the product obtained from reduction of the quinone with copper.[18] If the cobalt carbonyl reaction is carried out in hexane, a green product is obtained but, while characterization on this material remains incomplete, it is clearly not similar to the 9,10-phenanthrenequinone or 3,5-di-*tert*-butyl-1,2-benzoquinone products.



IV

Structural Features of $[Co(O_2C_6H_2(t\text{-}Bu)_2)_2]_4$. While the tris(semiquinone) complexes of trivalent vanadium, chromium, and iron have been shown to have monomeric, octahedral structures,[8] the bis complexes formed with divalent cobalt and nickel appear to have oligomeric structures with octahedrally coordinated metal ions. This has been confirmed in the case of $Co(O_2C_6H_2(t\text{-}Bu)_2)_2$, which has been found to be a centrosymmetric tetramer. A view of the complex molecule is shown in Figure 1 with a view of the inner coordination geometry shown in Figure 2. Bond lengths, bond angles, and least-squares planes for the ligands are given in Tables III–V. The four cobalt ions of the molecule are in a coplanar arrangement, which has been found for $[Ti(OC_2H_5)_4]_4$ and occurs typically for oxygen- and halogen-bridged tetrameric complexes. The $Co_4(NH(C_2H_4OH)_2)_2(NH(C_2H_4O)_2)_4^{2+}$ cation reported recently by Bertrand and co-workers[19] has this structural feature, and as a complex consisting of both divalent and trivalent cobalt ions, it serves as a clear example of how cobalt–oxygen bond lengths may be used to distinguish high-spin Co(II) from low-spin Co(III).

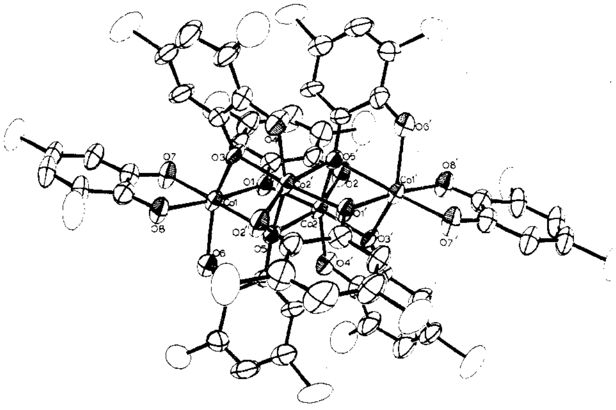


Figure 1. A view of the complete $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8$ complex molecule. Cobalt and oxygen atoms are shown with shaded ellipsoids. The prime symbol refers to atoms related to those in Table II by the crystallographic inversion center.

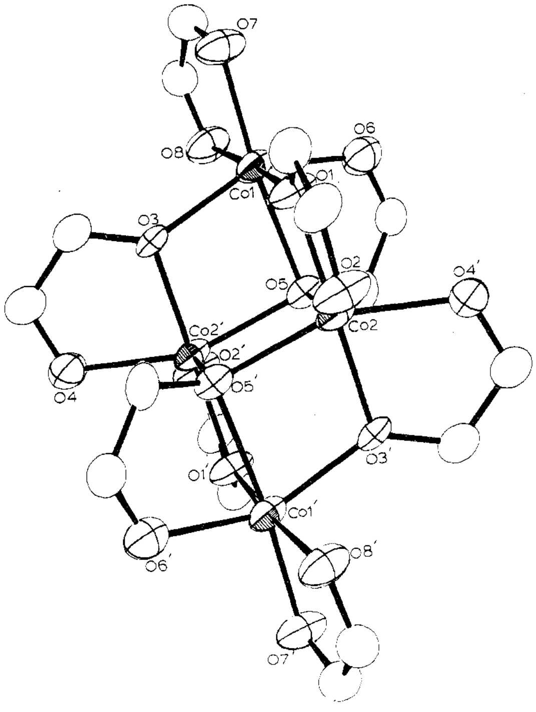


Figure 2. A view of the inner coordination sphere of the $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8$ molecule.

Ligand I of $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8$ bridges Co1 and Co2 through O1 and bonds terminally to Co2 through O2. This mode of coordination has been found for catecholate ligands in $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$ and semiquinones in $Mo_2O_5(O_2C_{14}H_8)_2$.[16] In both molybdenum structures the bridge is found to be quite unsymmetrical due to the effects of trans oxo ligands. Both cobalt lengths to O1 with values of 2.030 (4) and 2.076 (4) Å are quite similar and do not differ substantially from the Co2–O2 length of 2.042 (5) Å. Ligand II bonds in a similar manner with cobalt–oxygen lengths of 2.038 (4) and 2.074 (4) Å for the bridging oxygen O3 and 2.043 (5) Å for the terminal oxygen O4. Ligand III bonds terminally through O6 to Co1 with a length of 2.035 (5) Å, and bridges three metals Co1, Co2, and Co2′ through O5. Substantially longer Co–O lengths are found for O5: values of 2.133 (4) Å to Co2′, 2.175 (4) Å to Co2, 2.264 (4) Å to Co1. While triply bridged structures are known for oxo and alkoxide lig-

Table II. Positional and Thermal Parameters for the Atoms of $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8 \cdot 2C_6H_6$

atom	x	y	z	B_{11}[a]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co1	0.01414 (8)	0.07309 (7)	0.17930 (6)	3.30 (5)	2.30 (4)	2.70 (5)	1.40 (4)	0.70 (4)	−0.20 (4)
Co2	0.03247 (7)	−0.07423 (7)	0.03760 (6)	2.90 (4)	2.20 (4)	2.40 (4)	1.20 (4)	0.20 (4)	−0.40 (4)
O1	0.1054 (3)	0.0155 (3)	0.1662 (3)	2.8 (2)	3.4 (2)	2.7 (2)	1.8 (2)	0.0 (1)	−0.7 (2)
O2	0.1719 (4)	−0.0710 (3)	0.0819 (3)	3.9 (2)	4.2 (3)	3.5 (3)	2.4 (2)	0.2 (2)	−0.9 (3)
C1	0.1976 (5)	0.0284 (5)	0.2133 (5)	2.9 (4)	3.0 (4)	3.8 (4)	1.8 (3)	0.7 (3)	0.8 (4)
C2	0.2335 (6)	−0.0200 (5)	0.1648 (5)	3.2 (4)	3.1 (4)	4.2 (4)	1.8 (3)	0.8 (3)	0.2 (4)
C3	0.3333 (6)	−0.0104 (6)	0.2116 (6)	3.5 (4)	6.4 (5)	5.4 (5)	3.3 (4)	0.1 (4)	−0.2 (4)
C4	0.3897 (6)	0.0480 (7)	0.2992 (6)	3.3 (4)	6.7 (6)	5.7 (5)	3.0 (4)	−1.4 (4)	−0.2 (5)
C5	0.3537 (6)	0.0959 (6)	0.3468 (5)	4.3 (4)	4.5 (4)	3.8 (4)	2.1 (4)	−0.6 (4)	−0.4 (4)
C6	0.2594 (6)	0.0870 (5)	0.3025 (5)	4.0 (4)	3.8 (4)	2.3 (4)	1.9 (3)	−0.4 (3)	−0.3 (4)
C7	0.3727 (8)	−0.0609 (8)	0.1601 (7)	5.3 (6)	10.1 (8)	8.4 (6)	6.1 (6)	0.3 (5)	−1.5 (6)
C8	0.2995 (10)	−0.1688 (9)	0.1345 (8)	12.0 (9)	8.8 (7)	9.8 (7)	7.8 (7)	2.5 (6)	−0.4 (6)
C9	0.3797 (9)	−0.0274 (9)	0.0782 (8)	8.9 (8)	12.1 (9)	7.6 (6)	4.7 (6)	4.7 (6)	0.5 (6)
C10	0.4833 (9)	−0.0391 (12)	0.2262 (9)	7.2 (8)	20.9 (12)	13.5 (9)	10.3 (8)	−0.9 (6)	−4.9 (9)
C11	0.4260 (7)	0.1583 (7)	0.4466 (6)	4.6 (5)	6.4 (6)	4.4 (5)	2.4 (4)	−1.7 (4)	−1.4 (4)
C12	0.4437 (12)	0.0909 (11)	0.5065 (8)	15.9 (11)	15.0 (11)	5.6 (6)	10.5 (9)	−2.7 (6)	0.0 (7)
C13	0.5312 (9)	0.2398 (9)	0.4502 (8)	7.8 (8)	10.8 (8)	7.2 (6)	1.4 (6)	−1.6 (6)	−3.0 (6)
C14	0.3722 (10)	0.1988 (10)	0.4885 (8)	10.1 (9)	13.2 (10)	8.1 (7)	6.0 (8)	−3.1 (6)	−5.8 (7)
O3	0.0607 (3)	0.1607 (3)	0.0931 (3)	3.7 (2)	1.6 (2)	2.5 (3)	0.7 (2)	0.6 (1)	−0.4 (2)
O4	0.0450 (4)	0.2112 (3)	−0.0589 (3)	5.0 (2)	2.9 (2)	3.0 (3)	1.8 (2)	0.9 (2)	0.6 (2)
C15	−0.1105 (5)	−0.2550 (5)	−0.0990 (5)	2.9 (4)	2.8 (4)	3.5 (4)	1.0 (3)	1.2 (3)	0.0 (4)
C16	−0.1036 (6)	−0.2825 (5)	−0.0144 (5)	4.3 (4)	3.1 (4)	3.6 (4)	2.0 (3)	1.3 (3)	0.3 (4)
C17	−0.1597 (7)	−0.3850 (5)	−0.0152 (6)	6.8 (5)	1.9 (4)	5.3 (5)	1.5 (3)	2.3 (4)	0.6 (4)
C18	−0.2139 (8)	−0.4515 (6)	−0.0978 (6)	9.9 (7)	2.3 (4)	6.1 (6)	2.0 (4)	3.7 (5)	0.7 (4)
C19	−0.2224 (7)	−0.4262 (5)	−0.1812 (6)	6.8 (6)	2.1 (4)	5.5 (5)	−0.2 (4)	3.1 (4)	−0.8 (4)
C20	−0.1722 (6)	−0.3299 (5)	−0.1824 (5)	5.4 (4)	2.1 (4)	4.2 (4)	−0.1 (3)	1.8 (4)	0.0 (4)
C21	−0.1551 (9)	−0.4169 (7)	0.0739 (6)	10.6 (8)	5.0 (5)	6.0 (6)	4.5 (5)	3.3 (6)	2.8 (5)
C22	−0.1892 (10)	−0.3656 (8)	0.1285 (7)	13.0 (9)	7.1 (6)	6.9 (6)	4.0 (6)	5.6 (6)	4.1 (6)
C23	−0.0420 (11)	−0.3866 (9)	0.1315 (8)	13.5 (10)	9.7 (8)	9.5 (7)	7.5 (7)	3.4 (7)	5.9 (6)
C24	−0.2276 (11)	−0.5289 (7)	0.0559 (7)	17.1 (11)	3.5 (5)	8.4 (6)	3.0 (6)	6.0 (7)	3.4 (5)
C25	−0.2895 (10)	−0.5124 (7)	−0.2708 (7)	13.7 (10)	3.5 (5)	4.8 (6)	0.2 (6)	4.1 (6)	−0.8 (4)
C26	−0.2167 (15)	−0.5442 (12)	−0.2865 (12)	22.6 (17)	13.8 (12)	17.3 (11)	7.0 (11)	8.9 (11)	−8.0 (11)
C27	−0.3893 (12)	−0.5887 (10)	−0.2703 (8)	18.0 (12)	10.8 (9)	7.5 (7)	−9.8 (8)	6.5 (8)	−5.8 (7)
C28	−0.3154 (11)	−0.4772 (8)	−0.3501 (8)	13.9 (10)	5.3 (6)	7.1 (7)	−0.5 (6)	1.0 (7)	−3.1 (6)
O5	−0.0817 (3)	−0.0326 (3)	0.0376 (3)	2.6 (2)	2.5 (2)	2.6 (2)	1.1 (2)	0.6 (1)	−0.1 (2)
O6	−0.1094 (4)	−0.0465 (3)	0.1908 (3)	4.4 (2)	3.5 (2)	3.8 (3)	1.8 (2)	1.6 (2)	0.3 (2)
C29	0.1764 (5)	0.1020 (5)	−0.0324 (5)	2.6 (4)	2.2 (4)	4.3 (4)	1.0 (2)	1.5 (3)	1.0 (4)
C30	0.1894 (6)	0.1066 (5)	−0.1176 (5)	4.5 (4)	2.5 (4)	3.9 (4)	2.3 (3)	1.9 (4)	1.1 (4)
C31	0.2914 (6)	0.1776 (5)	−0.1165 (6)	4.5 (4)	3.1 (4)	6.0 (5)	1.6 (3)	3.1 (4)	1.1 (4)
C32	0.3688 (6)	0.2402 (6)	−0.0323 (6)	3.1 (4)	2.9 (4)	7.3 (4)	0.3 (3)	1.4 (4)	0.5 (4)
C33	0.3526 (6)	0.2385 (5)	0.0503 (5)	3.2 (4)	3.2 (4)	5.0 (4)	1.2 (3)	1.0 (4)	0.6 (4)
C34	0.2581 (5)	0.1692 (5)	0.0506 (5)	2.0 (4)	2.4 (4)	4.2 (4)	0.3 (2)	0.5 (3)	0.3 (4)
C35	0.3112 (8)	0.1791 (6)	−0.2048 (7)	7.1 (6)	4.5 (5)	8.9 (6)	1.6 (4)	5.8 (6)	1.4 (5)
C36	0.2878 (8)	0.0760 (7)	−0.2469 (7)	7.2 (6)	6.5 (6)	9.9 (6)	2.9 (4)	5.8 (6)	0.9 (6)
C37	0.2330 (10)	0.2051 (9)	−0.2742 (7)	13.6 (9)	10.8 (8)	5.7 (6)	7.0 (7)	5.0 (6)	4.7 (6)
C38	0.4257 (10)	0.2563 (9)	−0.1873 (9)	11.3 (9)	8.2 (7)	12.8 (8)	−0.2 (6)	9.9 (8)	0.2 (6)
C39	0.4465 (6)	0.3179 (6)	0.1371 (6)	3.1 (4)	3.8 (4)	6.8 (6)	−0.3 (3)	0.3 (4)	0.5 (4)
C40	0.4177 (7)	0.3096 (8)	0.2178 (6)	4.5 (5)	8.0 (6)	5.0 (5)	−2.2 (4)	0.0 (4)	0.2 (5)
C41	0.4784 (8)	0.4193 (7)	0.1238 (8)	7.7 (7)	3.7 (5)	10.0 (7)	0.0 (4)	0.2 (6)	0.1 (5)
C42	0.5404 (8)	0.3060 (9)	0.1521 (8)	5.1 (6)	10.4 (8)	9.8 (7)	3.5 (6)	−0.8 (5)	−0.5 (6)
O7	0.1018 (4)	0.1539 (3)	0.3108 (3)	4.9 (2)	4.3 (2)	2.9 (3)	3.2 (2)	0.5 (2)	−0.3 (3)
O8	−0.0651 (4)	0.1456 (3)	0.1923 (3)	4.4 (2)	3.7 (3)	2.6 (3)	2.7 (2)	0.9 (2)	−0.1 (2)
C43	0.0709 (6)	0.2086 (5)	0.3374 (5)	4.5 (4)	3.4 (4)	3.1 (4)	2.4 (3)	1.4 (4)	0.8 (4)
C44	−0.0196 (6)	0.2065 (5)	0.2706 (5)	4.7 (4)	3.2 (4)	3.3 (4)	1.8 (3)	1.7 (4)	0.9 (4)
C45	−0.0516 (7)	0.2725 (6)	0.2957 (5)	6.7 (5)	4.2 (4)	3.9 (4)	4.1 (4)	2.3 (4)	1.0 (4)
C46	0.0062 (7)	0.3333 (6)	0.3820 (5)	7.7 (6)	4.7 (4)	4.1 (4)	4.2 (4)	2.5 (4)	0.4 (4)
C47	0.0925 (7)	0.3354 (5)	0.4490 (5)	7.0 (6)	3.3 (4)	3.3 (4)	2.7 (4)	2.2 (4)	0.3 (4)
C48	0.1248 (6)	0.2739 (5)	0.4259 (5)	6.1 (5)	3.7 (4)	2.7 (4)	2.7 (4)	1.2 (4)	0.2 (4)
C49	−0.1446 (8)	0.2710 (7)	0.2245 (6)	8.7 (7)	7.0 (6)	5.4 (5)	6.4 (5)	2.4 (5)	1.1 (5)
C50	−0.2446 (8)	0.1687 (9)	0.1933 (7)	7.0 (6)	10.1 (8)	8.7 (6)	6.0 (6)	2.4 (6)	1.0 (6)
C51	−0.1608 (10)	0.3516 (8)	0.2671 (7)	13.8 (9)	10.0 (7)	8.1 (6)	10.1 (7)	4.0 (6)	2.3 (6)
C52	−0.1169 (9)	0.2989 (7)	0.1433 (6)	12.3 (8)	7.5 (6)	5.6 (5)	7.5 (6)	2.2 (5)	2.2 (5)
C53	0.1511 (8)	0.4096 (6)	0.5448 (5)	9.7 (7)	4.6 (5)	3.3 (4)	3.7 (4)	2.3 (4)	−0.3 (4)
C54	0.1898 (10)	0.5143 (7)	0.5337 (7)	14.7 (9)	4.0 (5)	7.5 (6)	2.9 (6)	4.1 (6)	0.3 (5)
C55	0.2472 (13)	0.4084 (10)	0.6022 (7)	19.2 (12)	12.1 (8)	5.1 (6)	10.8 (8)	−2.9 (7)	−4.4 (6)
C56	0.0789 (10)	0.3870 (9)	0.5933 (7)	14.3 (10)	9.2 (8)	6.8 (6)	3.1 (7)	7.1 (7)	−0.3 (6)
RC	0.153 (2)	−0.123 (2)	0.516 (2)	13.2 (15)	7.7 (12)	16.4 (12)	−0.9 (12)	5.9 (12)	−2.4 (12)
RC	0.145 (3)	−0.158 (2)	0.366 (2)	13.0 (14)	12.2 (12)	15.3 (12)	−4.1 (12)	4.7 (14)	−0.8 (13)
RC	0.090 (3)	−0.077 (2)	0.463 (3)	17.3 (14)	12.9 (12)	19.8 (12)	−6.9 (12)	−1.2 (13)	6.0 (13)
RC	0.208 (2)	−0.202 (2)	0.413 (4)	10.1 (14)	15.8 (11)	30.1 (11)	−0.5 (12)	8.2 (13)	−2.8 (13)
RC	0.085 (3)	−0.107 (3)	0.365 (3)	14.3 (15)	15.6 (12)	16.4 (12)	−5.2 (12)	2.7 (14)	7.3 (12)
RC	0.202 (3)	−0.171 (2)	0.502 (2)	14.4 (14)	12.2 (12)	16.0 (12)	0.9 (12)	4.7 (14)	0.6 (12)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ and is given in units of Å^2.

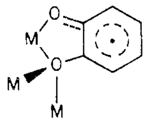
Table III. Bond Lengths (Å) for the $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8$ Complex Molecule

	Cobalt–Oxygen Bond Lengths		
Co1–O1	2.076 (4)	Co2–O1	2.030 (4)
Co1–O3	2.074 (4)	Co2–O2	2.042 (5)
Co1–O5	2.264 (4)	Co2–O3′	2.038 (4)
Co1–O6	2.035 (5)	Co2–O4′	2.043 (5)
Co1–O7	2.020 (4)	Co2–O5	2.175 (4)
Co1–O8	2.093 (4)	Co2–O5′	2.133 (4)
	Nonbonding Cobalt–Cobalt Separations		
Co1–Co1′	5.818 (2)	Co1–Co2′	3.317 (1)
Co1–Co2	3.305 (1)	Co2–Co2′	3.162 (2)
	Ligand I		
O1–C1	1.304 (7)	C3–C7	1.542 (11)
O2–C2	1.282 (7)	C5–C11	1.544 (10)
C1–C2	1.448 (9)	C7–C8	1.467 (14)
C2–C3	1.431 (9)	C7–C9	1.465 (14)
C3–C4	1.364 (10)	C7–C10	1.569 (13)
C4–C5	1.434 (11)	C11–C12	1.555 (14)
C5–C6	1.354 (10)	C11–C13	1.508 (14)
C6–C1	1.388 (9)	C11–C14	1.538 (15)
	Ligand II		
O4–C16	1.282 (7)	C19–C25	1.561 (11)
O3–C15	1.297 (7)	C17–C21	1.540 (11)
C15–C16	1.439 (10)	C21–C22	1.516 (13)
C16–C17	1.433 (9)	C21–C23	1.521 (14)
C17–C18	1.351 (10)	C21–C24	1.528 (12)
C18–C19	1.406 (11)	C25–C26	1.521 (20)
C19–C20	1.351 (10)	C25–C27	1.450 (15)
C20–C15	1.414 (9)	C25–C28	1.450 (15)
	Ligand III		
O6–C30	1.277 (7)	C31–C35	1.534 (11)
O5–C29	1.328 (7)	C35–C36	1.544 (12)
C29–C30	1.438 (9)	C35–C37	1.614 (14)
C30–C31	1.440 (10)	C35–C38	1.523 (13)
C31–C32	1.382 (10)	C33–C39	1.544 (10)
C32–C33	1.417 (11)	C39–C40	1.486 (12)
C33–C34	1.357 (9)	C39–C41	1.498 (12)
C34–C29	1.403 (9)	C39–C42	1.515 (13)
	Ligand IV		
O8–C44	1.272 (7)	C45–C49	1.532 (11)
O7–C43	1.282 (7)	C47–C53	1.551 (10)
C43–C44	1.467 (10)	C49–C50	1.519 (13)
C43–C48	1.413 (9)	C49–C51	1.564 (11)
C47–C48	1.371 (10)	C49–C52	1.521 (12)
C46–C47	1.422 (10)	C53–C54	1.522 (12)
C45–C46	1.360 (10)	C53–C55	1.507 (15)
C44–C45	1.440 (9)	C53–C56	1.480 (13)

Table IV. Bond Angles (deg) for the $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8$ Complex Molecule

	Angles about Co1		
O1–Co1–O3	90.1 (1)	O3–Co1–O8	85.1 (2)
O1–Co1–O5	76.6 (1)	O5–Co1–O6	74.9 (2)
O1–Co1–O6	101.1 (2)	O5–Co1–O7	172.9 (2)
O1–Co1–O7	98.4 (2)	O5–Co1–O8	105.6 (2)
O1–Co1–O8	173.9 (2)	O6–Co1–O7	101.5 (2)
O3–Co1–O5	75.2 (2)	O6–Co1–O8	85.0 (2)
O3–Co1–O6	144.5 (2)	O7–Co1–O8	79.9 (2)
O3–Co1–O7	110.1 (2)		
	Angles about Co2		
O1–Co2–O2	79.0 (2)	O2–Co2–O5′	94.8 (2)
O1–Co2–O3′	170.6 (2)	O3′–Co2–O4′	78.8 (2)
O1–Co2–O4′	101.6 (2)	O3′–Co2–O5	90.9 (2)
O1–Co2–O5	79.6 (2)	O3′–Co2–O5′	78.9 (2)
O1–Co2–O5′	100.8 (2)	O4′–Co2–O5	97.6 (2)
O2–Co2–O3′	110.4 (2)	O4′–Co2–O5′	157.5 (2)
O2–Co2–O4′	78.8 (2)	O5–Co2–O5′	85.5 (2)
O2–Co2–O5	158.2 (2)		
	Ligand I		
Co1–O1–C1	137.8 (4)	C3–C4–C5	124.5 (7)
Co2–O1–C1	114.5 (4)	C4–C5–C6	119.3 (7)
Co2–O2–C2	113.9 (4)	C5–C6–C1	119.3 (7)
O1–C1–C2	115.2 (6)	C6–C1–C2	121.7 (7)
O1–C1–C6	123.0 (6)	C2–C3–C7	119.2 (7)
O2–C2–C1	117.2 (6)	C4–C3–C7	124.5 (7)
O2–C2–C3	123.8 (7)	C4–C5–C11	118.4 (7)
C1–C2–C3	118.9 (7)	C6–C5–C11	112.3 (7)
C2–C3–C4	116.0 (7)		
	Ligand II		
Co1–O3–C15	136.3 (4)	C17–C18–C19	124.3 (7)
Co2–O3–C15	113.4 (4)	C18–C19–C20	120.3 (7)
Co2–O4–C16	114.1 (4)	C19–C20–C15	119.4 (7)
O3–C15–C16	116.6 (6)	C20–C15–C16	119.4 (7)
O3–C15–C20	123.9 (7)	C16–C17–C21	121.4 (7)
O4–C16–C15	116.4 (6)	C18–C17–C21	122.2 (7)
O4–C16–C17	123.5 (7)	C18–C19–C25	117.8 (7)
C15–C16–C17	120.1 (7)	C20–C19–C25	121.8 (8)
C16–C17–C18	116.4 (7)		
	Ligand III		
Co1–O5–C29	109.7 (4)	C30–C31–C32	116.3 (7)
Co2–O5–C29	118.7 (4)	C31–C32–C33	124.0 (7)
Co2′–O5–C29	132.8 (4)	C32–C33–C34	120.1 (7)
Co1–O6–C30	117.9 (4)	C33–C34–C29	118.8 (7)
O5–C29–C30	115.9 (6)	C34–C29–C30	121.8 (6)
O5–C29–C34	122.3 (6)	C30–C31–C35	120.4 (7)
O6–C30–C29	118.1 (6)	C32–C31–C35	123.2 (8)
O6–C30–C31	123.2 (7)	C32–C33–C39	116.7 (7)
C29–C30–C31	118.8 (7)	C34–C33–C39	123.1 (7)
	Ligand IV		
Co1–O7–C43	113.5 (4)	C45–C46–C47	126.0 (7)
Co1–O8–C44	111.7 (4)	C46–C47–C48	118.7 (7)
O7–C43–C44	117.6 (6)	C47–C48–C43	119.7 (7)
O7–C43–C48	122.1 (7)	C48–C43–C44	120.2 (7)
O8–C44–C43	117.6 (7)	C44–C45–C49	118.7 (6)
O8–C44–C45	123.6 (7)	C46–C45–C49	125.3 (7)
C43–C44–C45	119.3 (6)	C46–C47–C53	120.0 (7)
C44–C45–C46	116.0 (7)	C48–C47–C53	121.3 (8)

ands, they have not been observed previously for catecholates or semiquinones. Ligand IV of the molecule is chelated to Co1 with cobalt–oxygen lengths of 2.020 (4) and 2.093 (4) Å. The shorter of these two lengths, which is also the shortest Co–O length of the molecule, occurs at the site located trans to the long Co1–O5 bond. The average Co–O length calculated excluding the anomalously long lengths to O5 is 2.05 (2) Å and is consistent with high-spin Co(II). This formulation requires that the ligands of the molecule bond formally as semiquinones. Electron spin resonance experiments on semiquinone complexes show very weak coupling to the metal ion, indicating that the unpaired electron is localized in a ligand electronic level which contributes little to bonding with the metal.[7,20] The EPR spectrum of the uncomplexed 3,5-di-*tert*-butyl-1,2-semiquinone radical anion shows coupling of approximately 3 G with the ring proton at the 4 position and weaker coupling (~0.3 G) with the *tert*-butyl protons at the 5 position. No interaction is observed with the 6-proton or the 3-*tert*-butyl group. These results with similar studies carried out on other substituted *o*-semiquinones show that there is considerable concentration of spin density at the carbon–carbon bond opposite to the carbon–oxygen bonds. Consequently, a semiquinone ligand with its unpaired electron contained in an orbital which is essentially nonbonding with respect to the bond with the metal ion would donate at most two electron pairs per oxygen. For one oxygen atom to bond with three metals, a more localized radical anion structure would be required which would place the negative charge on that oxygen to provide three electron pairs (V). A contribution from this localized electronic structure may be detectable in the structural features of ligand III.



V

Table V. Least-Squares Planes for $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8$

Ligand I

Plane: $3.10x + 11.45y - 9.38z = 1.05$

atom	dist, Å	atom	dist, Å
O1	−0.002 (5)	C4	0.005 (10)
O2	0.004 (5)	C5	−0.004 (8)
C1	−0.009 (7)	C6	0.017 (8)
C2	0.002 (7)	C7	0.009 (13)
C3	−0.018 (9)	C11	0.001 (10)

Ligand II

Plane: $15.56x - 8.21y - 4.08z = 0.77$

atom	dist, Å	atom	dist, Å
O3	0.025 (7)	C18	0.007 (12)
O4	−0.013 (5)	C19	0.008 (14)
C15	−0.002 (10)	C20	−0.032 (12)
C16	0.009 (9)	C21	−0.062 (17)
C17	0.004 (10)	C25	0.037 (18)

Ligand III

Plane: $10.94x - 15.13y + 1.20z = 0.33$

atom	dist, Å	atom	dist, Å
O5	−0.062 (6)	C32	0.037 (11)
O6	0.029 (6)	C33	−0.015 (11)
C29	0.021 (9)	C34	0.000 (9)
C30	−0.008 (10)	C35	0.124 (14)
C31	0.035 (12)	C39	−0.085 (14)

Ligand IV

Plane: $7.31x + 7.94y - 10.35z = 1.29$

atom	dist, Å	atom	dist, Å
O7	−0.022 (5)	C47	0.026 (10)
O8	0.039 (5)	C48	0.014 (9)
C43	−0.016 (8)	C49	0.060 (11)
C44	−0.028 (8)	C53	0.007 (10)
C45	−0.032 (8)	Co1	0.116
C46	−0.020 (9)		

Semiquinone ligands characterized structurally for $Cr(O_2C_6Cl_4)_3$,[21] $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3$,[22] $Fe(O_2C_{14}H_8)_3$,[8] and $Mo_2O_5(O_2C_{14}H_8)_3$[16a] all have carbon–oxygen lengths in the 1.29 (1) Å range with little variation. Chelated catecholate ligands characterized structurally for $[Mo(O_2C_6Cl_4)_3]_2$,[9] $Fe(O_2C_6H_4)_3{}^{3-}$,[23] $Cr(O_2C_6H_4)_3{}^{3-}$,[23] $[MoO(O_2C_6H_2(t\text{-}Bu)_2)_2]_2$, $Pd(PPh_3)_2(O_2C_6Cl_4)$,[24] and $Mo(O_2C_{14}H_8)_3$[25] have carbon–oxygen lengths of 1.35 (1) Å, also with little variation. The average C–O length of 1.285 (11) Å for the $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8$ molecule, calculated excluding the C29–O5 length, is quite consistent with the semiquinone formulation for the ligands. A second feature which is distinctive for semiquinone ligands is a carbon–carbon length of 1.44 (1) Å for the bond between quinone carbon atoms. Catecholates have an aromatic value of 1.40 (1) Å at this position. In the present structure, the average value is 1.448 (7) Å. The structural features of ligand III with the triply bridged oxygen O5 are not significantly different from the other three ligands with the exception of the C29–O5 bond length. Its value of 1.328 (7) Å approaches the value associated with chelated catecholate ligands and reflects a clear contribution from the localized electronic structure V.

The related nickel complex crystallized from both toluene and benzene has been found to be isomorphous and isostructural with $Co_4(O_2C_6H_2(t\text{-}Bu)_2)_8$. This is reasonable since Ni(II)–O lengths are quite similar to Co(II)–O values and the structural features of the ligands would not be expected to change.

Magnetic Properties of the Bis(semiquinone) Oligomers of Co(II) and Ni(II). The magnetic properties of the tris(semiquinone) complexes of Cr(III) and Fe(III) show an interesting temperature dependence which has been attributed to an antiferromagnetic exchange interaction between the paramagnetic ligands and unpaired electrons on the metal ions.[8] Room-temperature moments of 3.96, 3.43, and 2.95 μ_B (285 K) have been reported for $Fe(O_2C_6Cl_4)_3$, $Fe(O_2C_{14}H_8)_3$, and $Fe(O_2C_6H_2(t\text{-}Bu)_2)_3$, respectively. At 4.2 K, values of 2.14, 1.52, and 2.66 μ_B are observed for this series, reflecting an $S = 1$ ground state with a contribution from an intermolecular exchange mechanism apparent from the anomalously low values of the tetrachloro-1,2-semiquinone and 9,10-phenanthrenesemiquinone complexes. This is in accord with the structural features of these complexes which show intermolecular stacking in their solid-state structures. A similar pattern is observed for the tris(semiquinone)chromium(III) complexes where weak paramagnetism (~1.0 μ_B) is observed at room temperature for compounds prepared with the more electrophilic quinones and diamagnetism for the fully coupled $Cr(O_2C_6H_2(t\text{-}Bu)_2)_3$ complex molecule.

Table VI. Room-Temperature Magnetic Susceptibilities of Oligomeric Bis(semiquinone) Complexes of Co(II) and Ni(II)

complex	μ_{eff}, μ_B
$Co(O_2C_{14}H_8)_2$	4.67[a]
$Co(O_2C_6H_2(t\text{-}Bu)_2)_2$	4.75[a]
$Ni(O_2C_6Cl_4)_2$	3.49[b]
$Ni(O_2C_{14}H_8)_2$	3.06[a]
$Ni(O_2C_6H_2(t\text{-}Bu)_2)_2$	3.92,[b] 2.90[c]

[a] This work. [b] Reference 11. [c] Reference 26.

Spectral similarities between the tris complexes above and the neutral bis complexes of Co and Ni suggest that these also may be regarded as complexes of semiquinone ligands with divalent metal ions. This is further substantiated by the results of the $[Co(O_2C_6H_2(t\text{-}Bu)_2)_2]_4$ structure determination. As such, temperature-dependent paramagnetism may also be observed for these compounds, although the complexity of the tetrameric cobalt complex molecule may greatly complicate interpretation of magnetic data in terms of individual exchange mechanisms. In the absence of any significant metal–semiquinone coupling an $S = {}^5/_2$ moment would be expected per metal ion for the Co^{2+} complexes and an $S = 2$ moment for the Ni^{2+} compounds. Fully coupled complexes would show $S = {}^1/_2$ and $S = 0$ ground states for the Co^{2+} and Ni^{2+} compounds, respectively. Room-temperature magnetic susceptibility data for two cobalt and three nickel complexes are contained in Table VI. The values of the two cobalt complexes are similar but those for the nickel complexes vary over the range of 1 μ_B. This is particularly significant for $Ni(O_2C_6H_2(t\text{-}Bu)_2)_2$. A value of 3.92 μ_B per nickel was originally reported by Holm, and we have been able to reproduce this value for $Ni_4(O_2C_6H_2(t\text{-}Bu)_2)_8\cdot 2C_6H_5CH_3$. It differs from the moment of the isostructural cobalt complex by 0.83 μ_B, despite the electronic difference of one spin per metal center. Razuvaev has reported a monomeric form of the complex which has a moment of 2.90 μ_B per nickel.[26] This monomer would be similar to the square-planar bis(*o*-phenylenediamino)nickel complex, $Ni(C_6H_4(NH)_2)_2$, which is reported to be diamagnetic.[27] The magnetic difference between the 9,10-phenanthrenesemiquinone complexes is 1.61 μ_B, more consistent with their electronic difference. The moments of all compounds in Table VI suggest spin–spin coupling but remain well above the limiting spin-paired values. They may, therefore, show interesting temperature-dependent magnetic behavior as found for the Fe and Cr complexes. Interpretation of magnetic data may prove to be substantially more challenging for the oligomeric bis(semiquinone) complexes than for the octahedral tris complexes of Fe and Cr.

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Registry No. $[Co(O_2C_6H_2(t\text{-}Bu)_2)_2]_4\cdot 2C_6H_6$, 71370-71-3; $Co(O_2C_{14}H_8)_2$, 41173-19-7; $Ni(O_2C_{14}H_8)_2$, 41173-20-0.

Supplementary Material Available: Listing of structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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A Centric Organic Disulfide (C–S–S–C = 180°): Crystal and Molecular Structures of Chloro[bis(2-pyrimidyl) disulfide]copper(I) Monohydrate and of Bis(2-pyrimidyl) Disulfide[1]

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The crystal and molecular structures of chloro[bis(2-pyrimidyl) disulfide]copper(I) monohydrate, $Cu(C_8H_6N_4S_2)Cl\cdot H_2O$, and of bis(2-pyrimidyl) disulfide, $C_8H_6N_4S_2$, have been determined by single-crystal X-ray diffraction techniques using 2401 and 1873 unique reflections, respectively. These structures were refined by full-matrix least-squares procedures to final conventional R indices of 0.039 and 0.036, respectively. Counter methods and monochromatized Mo Kα radiation were employed. The complex crystallizes in the monoclinic space group $C2/m$ with a = 11.916 (3) Å, b = 17.405 (4) Å, c = 6.642 (2) Å, and β = 116.58 (2)° and with 4 formula units per unit cell. The ligand crystallizes in the triclinic space group $P\bar{1}$ with a = 9.673 (5) Å, b = 15.033 (6) Å, c = 7.045 (3) Å, α = 98.73 (3)°, β = 100.02 (4)°, and γ = 86.45 (4)° and with 4 molecules per unit cell. In the complex, ligand molecules bridge between Cu(I) ions to form polymeric sheets. Each Cu(I) ion is coordinated by two chloride ions and by two nitrogen atoms from two bis(2-pyrimidyl) disulfide ligand molecules, forming a distorted tetrahedron with coordination angles ranging from 95.7 to 142.2°. The chloride ions bridge between pairs of Cu(I) ions to form rhombic $\overline{\mathrm{CuClCuCl}}$ rings. The relatively short Cu^{I}–N bond distance, 1.966 (3) Å, indicates strong d → π^* back-bonding from the Cu(I) d orbitals into the lowest lying π^* molecular oribtal of each pyrimidine ring. The most unusual structural feature of the complex is the C–S–S–C torsion angle of 180° (by symmetry), a value not heretofore reported for an organic disulfide. This unusual torsion angle is stabilized by a π system which extends over the entire planar ligand, although the π component of the S–S bond is small. In this conformation, the repulsive forces between the sulfur $3p_\pi$ lone-pair electrons and those of the nitrogens on adjacent rings are largely eliminated. Repulsions between the sulfur atoms are at a maximum, however, accounting for the long S–S bond distance of 2.113 (1) Å. The two independent molecules in the structure of the free ligand have normal C–S–S–C torsion angles (83.9 and 85.4°) and normal S–S bond lengths (2.017 (2) and 2.020 (2) Å) for aromatic disulfides in the equatorial conformation (N–C–S–S torsion angle near 0°).

Introduction

The first crystal structure determination of a metal ion complexed to an organic disulfide, that of chloro(diethyl disulfide)copper(I),[2a] showed the presence of tetrahedral copper(I) ions each bonded to two chloride ions in continuous –Cu–Cl– chains and to two sulfur atoms, one from each of two disulfide groups. This indicated that a sulfur atom of a disulfide group could act as a ligand. Other copper(I)–disulfide complexes whose crystal structures have been determined[2b-d] also show direct coordination of sulfur to tetrahedral Cu(I). To investigate this effect further, we prepared the complex reported herein and determined its crystal structure. Although sulfur does not coordinate to copper(I), the disulfide ligand is found in a conformation not heretofore reported.

Experimental Section

Syntheses. Cupric chloride dihydrate, cupric perchlorate hexahydrate (99.9%), and 2-pyrimidinethiol (alternative name: 2-mercaptopyrimidine) were obtained from Mallinckrodt Chemical Works, Gallard-Schlessinger Chemical Manufacturing Corp., and Aldrich Chemical Co., respectively. All other chemicals were of

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