(15) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970); see also "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1975, Table 2.3.1, pp 149–150.
(16) J. Karle and I. L. Karle, *Acta Crystallogr.*, **21**, 849 (1966).
(17) This technique was demonstrated initially by Ibers and co-workers (see ref 18–20) and has been used extensively by Bau and co-workers (cf. ref 21).
(18) J. A. Ibers and D. T. Cromer, *Acta Crystallogr.*, **11**, 794 (1958).
(19) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).
(20) R. J. Doedens, W. T. Robinson, and J. A. Ibers, *J. Am. Chem. Soc.*, **89**, 4323 (1967).
(21) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.*, **95**, 4532 (1973).
(22) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 1139 (1963); **23**, 558 (1967).
(23) A. C. Larson in "Crystallographic Computing", F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 251 ff.
(24) Note that $(-\mathrm{d} \ln T)/\mathrm{d}\mu = \bar{t}$ (the weighted-average path length (in mm) of x-rays through the crystal).
(25) Supplementary material.
(26) σ(ext) and σ(av) are defined in footnotes to Table VIII.
(27) M. R. Churchill and K. G. Lin, *Inorg. Chem.*, **14**, 1675 (1975).
(28) L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Am. Chem. Soc.*, **92**, 7312 (1970).
(29) M. R. Churchill and S. W. Ni, *J. Am. Chem. Soc.*, **95**, 2150 (1973).
(30) J. P. Olsen, T. F. Koetzle, S. W. Kirtley, M. Andrews, D. L. Tipton, and R. Bau, *J. Am. Chem. Soc.*, **96**, 6621 (1974).
(31) M. R. Churchill and S. W. Chang, *Inorg. Chem.*, **13**, 2413 (1974).
(32) R. Mason and D. M. P. Mingos, *J. Organomet. Chem.*, **50**, 53 (1973).
(33) B. K. Teo, M. B. Hall, R. F. Fenske, and L. F. Dahl, *J. Organomet. Chem.*, **70**, 413 (1974).
(34) At no point in this discussion will we consider the problem of differentiating between symmetric or asymmetric M–H–M bonds. There is no evidence for asymmetric bonds but no proof that they do not occur.
(35) A. S. Foust, W. A. G. Graham, and R. P. Stewart, *J. Organomet. Chem.*, **54**, C22 (1973).
(36) M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).
(37) R. P. White, T. E. Block, and L. F. Dahl, unpublished work. Some details are given in ref 28 of the present paper.
(38) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Am. Chem. Soc.*, **90**, 7135 (1968).
(39) S. W. Kirtley, H. D. Kaesz, M. R. Churchill, and C. Knobler, unpublished work.
(40) M. J. Bennett, W. A. G. Graham, J. K. Hoyano, and W. L. Hucheon, *J. Am. Chem. Soc.*, **94**, 6232 (1972).
(41) P. Dapporto, S. Midollini, and L. Sacconi, *Inorg. Chem.*, **14**, 1643 (1975).
(42) J. Potenza, P. Giordano, D. Mastropaolo, and A. Efraty, *Inorg. Chem.*, **13**, 2540 (1974).
(43) M. R. Churchill and J. Wormald, *J. Am. Chem. Soc.*, **93**, 5670 (1971).
(44) R. D. Wilson and R. Bau, *J. Am. Chem. Soc.*, submitted for publication.
(45) A. Simon, *Z. Anorg. Allg. Chem.*, **355**, 311 (1967).
(46) M. J. Mays and R. N. F. Simpson, *J. Chem. Soc. A*, 1444 (1968).
(47) J. W. White and C. J. White, *J. Chem. Soc. A*, 2843 (1971).
(48) B. T. Huie, C. B. Knobler, and H. D. Kaesz, *J. Chem. Soc., Chem. Commun.*, 684 (1975).
(49) R. Bau, B. Don, R. Greatrex, R. J. Haines, R. A. Love, and R. D. Wilson, *Inorg. Chem.*, **14**, 3021 (1975).
(50) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).
(51) F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 4155 (1974); see also C. H. Wei and L. F. Dahl, *ibid.*, **91**, 1351 (1969).
(52) G. M. Sheldrick and J. P. Yesinowski, *J. Chem. Soc., Dalton Trans.*, 873 (1975).
(53) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 778 (1968).
(54) M. R. Churchill, B. G. DeBoer, J. R. Shapley, and J. B. Keister, *J. Am. Chem. Soc.*, **98**, 2357 (1976).

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Transition Metal Ions in High Formal Oxidation States. Structural Characterization of the Nickel and Copper Complexes of the 1,1-Dicarboethoxy-2,2-ethylenedithiolate Ligand

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Bis(trimethylphenylammonium) bis(1,1-dicarboethoxy-2,2-ethylenedithiolato)nickelate(II), $((CH_3)_3(C_6H_5)N)_2Ni(S_2C{=}C(COOC_2H_5)_2)_2$ (A), crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell. The cell dimensions are $a = 9.032$ (3) Å, $b = 8.716$ (4) Å, $c = 15.532$ (6) Å, $\alpha = 82.04$ (2)°, $\beta = 114.73$ (2)°, and $\gamma = 114.48$ (2) Å. Potassium bis(1,1-dicarboethoxy-2,2-ethylenedithiolato)cuprate(III) etherate, $KCu(S_2C{=}C(COOC_2H_5)_2)_2{\cdot}O(C_2H_5)_2$ (B), crystallizes in the monoclinic space group $C2/c$ with four molecules per unit cell. The cell dimensions are $a = 13.781$ (3) Å, $b = 17.527$ (3) Å, $c = 12.903$ (2) Å, and $\beta = 107.21$ (1)°. Intensity data for both A and B were collected with a four-circle computer-controlled diffractometer using the θ–2θ scan technique. All 25 nonhydrogen atoms in A were refined anisotropically and the 24 hydrogen atoms were included as fixed atoms. In B one of the ligand ethyl groups and the unique ether ethyl group were constrained to refine as groups of fixed geometry. Of the remaining nonhydrogen atoms only the copper, sulfurs, and the carbonyl oxygen atoms were refined anisotropically. Refinement by full-matrix least squares on 451 data for A and 1571 data for B gave final R values of 0.038 for A and 0.060 for B. The geometry of the MS_4 moiety in both structures is square. Average values of selected bond distances and bond angles are as follows: for A, Ni–S = 2.195 (2) Å, S–S(intraligand) = 2.789 (2) Å, S–S(interligand) = 3.389 (2) Å, S–Ni–S(intraligand) = 78.90 (6)°, S–Ni–S(interligand) = 101.10 (6)°; for B, Cu–S = 2.195 (5) Å, S–S(intraligand) = 2.766 (6) Å, S–S(interligand) = 3.407 (8) Å, S–Cu–S(intraligand) = 78.14 (24)°, S–Cu–S(interligand) = 101.87 (23)°. A plot of normalized differences between corresponding structural parameters of the ligands in the two structures vs. the expected values of a normal distribution of random errors indicates systematic differences in the ligand structural parameters and a higher localization of charge on the sulfurs in B. These data and the identical M–S bond lengths in both structures suggest that in B the oxidation is centered in the Cu–S chromophore.

Introduction

One of the most interesting characteristics of coordination compounds with sulfur-containing ligands is the diversity of their redox properties. Detailed studies by various investigators[1] have indicated that the reversible oxidations observed with a variety of 1,2-dithiolate complexes[2] involve molecular orbitals whose metal and ligand characters vary with the type of ligand. With certain 1,1-dithiolates[3] irreversible oxidations give rise to sulfur-rich species[4] in which sulfur insertion results in an expansion of the metal–ligand four-membered ring.[5]

Recent electrochemical studies have shown that the dithiocarbamate complexes undergo reversible oxidation state changes.[6] Synthetic and x-ray studies indicate that the

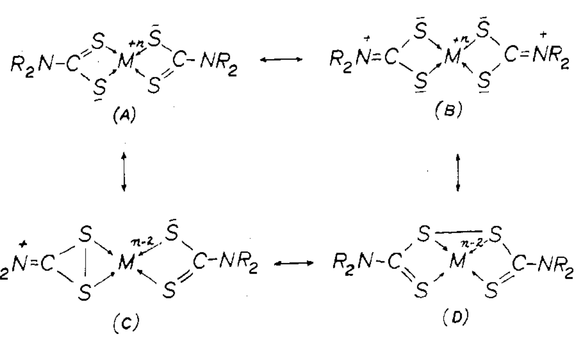

Figure 1. Valence tautomers in oxidized metal dithiocarbamate complexes.

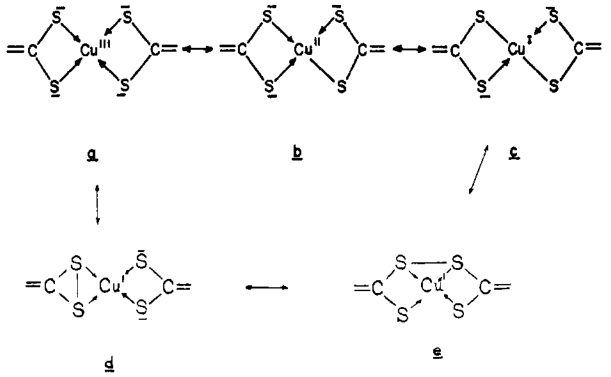

Figure 2. Possible resonance forms of $Cu^{III}(DED)_2^-$.

tris(dithiocarbamato) complexes $M(R_2dtc)_3^+$, M = Fe, Mn, and Ni, can be described, at least formally, as Fe(IV),[7,8] Mn(IV),[9] and Ni(IV)[10] complexes, respectively. Similarly the planar $Cu^{III}(R_2dtc)_2^+$ complex has been isolated[11] and structurally characterized.[12]

The ability of the dithiocarbamate ligands to stabilize metal ions in high formal oxidation states has been rationalized in terms of (a) a delocalization of charge on the ligand[13] (Figure 1B) and (b) S–S interligand interactions[10] (Figure 1D).

Recently we reported[14] on the synthesis and structural characterization of a new class of oxidized 1,1-dithiolate complexes of copper and iron with the 1,1-dicarboethoxy-2,2-ethylenedithiolate ligand (DED^{2-}). By contrast to the previously studied[4] oxidized 1,1-dithiolate complexes, no sulfur addition was detected on the coordinated (DED^{2-}) ligand which instead maintained its structural integrity following oxidation. The existence of unusually high oxidation states of the DED complexes must be explained, then, as a consequence of any of the following reasons: (a) S–S interactions, (b) oxidation of the metal ion, and (c) covalency in the M–S bond (Figure 2).

Our structural studies on the DED complexes were initiated[14] in an attempt to explore in detail the nature of M–S interactions in these complexes. An additional impetus for these studies was provided by the fact that a better understanding of the M–S bond is needed for the interpretation of the redox activity of certain copper- and iron-containing enzymes. For example, the nature of the "EPR-inactive Cu^{2+}", a proposed electron-accepting site in various multicopper blue oxidases[15] and cytochrome *c* oxidase,[16] has been the subject of considerable discussion. A suggested model[17] that appears to be in accord with various experimental observation is a copper–mercaptide redox center. In this model the state of copper is indeterminable, in that the copper–sulfur interaction can be regarded either as a copper(I)–disulfide coordination or as a Cu^{2+} covalently bound to a mercaptide function (i.e., a Cu^{2+}-stabilized "sulfur radical"). The valence tautomers considered in this model are analogous to forms b and d of Figure 2.

Table I. Crystal Intensity Measurement and Structure Determination Data for the $M(S_2CC(COOC_2H_5)_2)_2^{n-}$ Complexes

	$KCu(S_2C_8O_4H_{10})_2\cdot O(C_2H_5)_2$	$((CH_3)_3(C_6H_5)N)_2Ni(S_2C_8O_4H_{10})_2$
Mol wt	645.0	799.1
a, Å	13.781 (3)	9.032 (3)
b, Å	17.527 (3)	8.716 (4)
c, Å	12.903 (2)	15.532 (6)
α, deg	90.00	82.04 (2)
β, deg	107.21 (1)	114.73 (2)
γ, deg	90.00	114.48 (2)
d(obsd), g cm^{-3}	1.70 (5)[a]	1.26 (4)[b]
d(calcd), g cm^{-3}	1.44	1.32
Z	4	1
Space group	$C2/c$[c]	$P\bar{1}$[d]
λ(Mo Kα), Å	0.7107	0.7107
μ, cm^{-1}	12.10	7.28
Crystal dimensions, mm	0.10 × 0.10 × 0.22	0.20 × 0.22 × 0.34
Reflections measd	1311	2059
Takeoff angle, deg	3.5	3.5
2θ range, deg	$0 < 2\theta < 30$	$0 < 2\theta < 40$
Unique reflections	608	1897
Final R_1[e]	0.060	0.038
Final R_2[f]	0.068	0.053
Reflections used in refinement[g]	451	1571
SDOUW[h]	2.12	1.85

[a] Measured by flotation in CCl_4/benzene mixture. It is probable that the bulk density of the sample is greater than that of the crystallographic grade crystals due to loss or replacement of the ether of crystallization. [b] Measured pycnometrically. [c] Systematic absences: hkl, $h + k \neq 2n$; $h0l$, $l \neq 2n$. The choice of the centric space group was confirmed by the successful refinement of the structure. [d] The choice of the centric space group was confirmed following the successful refinement of the structure. [e] $R_1 = \Sigma|\Delta F|/\Sigma|F_o|$. [f] $R_2 = [\Sigma w(\Delta F)^2/\Sigma w|F_o|^2]^{1/2}$. [g] Criterion for acceptance: $F^2 \geqslant 3\sigma(F^2)$. [h] Standard deviation of an observation of unit weight ("goodness of fit"); $(\Sigma w(\Delta|F|)^2/(n_o - n_p))^{1/2}$

In this paper we report in detail the structural characterization of the isoelectronic $M(DED)_2^{n-}$ complexes (M = Cu, *n* = 1; M = Ni, *n* = 2) and our findings concerning the nature of the M–S bond in these complexes.

Experimental Section

X-Ray Diffraction Measurements. Collection and Reduction of Data. Specific details concerning crystal characteristics and x-ray diffraction methodology are shown in Table I.

Intensity data for both compounds were obtained on a Picker-Nuclear four-circle diffractometer equipped with a scintillation counter and pulse height analyzer and automated by a DEC PDP 8-I computer and disk with FACS-I DOS software. Graphite monochromatized Mo Kα radiation ($2\theta_m$ = 12.50°) was used for data collection and cell dimension measurements (K$\bar{\alpha}$; λ 0.7107 Å). Intensity data were collected using a θ–2θ scan technique with a scan rate of 1°/min in 2θ. The scan width was centered on the predicted position of the Mo $K\alpha_1$ peak and expanded at the high-2θ end to allow for α_1–α_2 separation at higher angles. Stationary-crystal, stationary-counter background measurements were made for 10 s at each end of the scan range. Three reflections well separated in reciprocal space were measured after every 100 data measurements to monitor crystal and instrumental stability.

The raw data were reduced to net intensities,[18] estimated standard deviations were calculated on the basis of counting statistics, Lorentz–polarization corrections and decay corrections (where applicable) were applied, and equivalent reflections were averaged.[18] The estimated standard deviation of the structure factor was taken as the larger of that derived from counting statistics and that derived from scatter of multiple measurements.

Table II

a. Positional and Thermal Parameters of Atoms in $KCu(DED)_2{\cdot}OEt_2$

Atom	x	y	z	B_{11}[b]	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.25	0.25	0.00	8.9 (2)	6.1 (3)	7.3 (2)	−0.7 (2)	2.8 (2)	0.4 (2)
K	0.00	0.3882 (4)	0.25	9.2 (4)	6.7 (5)	8.1 (4)	0.0	4.2 (3)	0.0
S(1)	0.1763 (4)	0.3306 (3)	0.0835 (4)	10.1 (4)	7.1 (4)	8.3 (3)	−1.2 (3)	4.3 (3)	0.7 (3)
S(2)	0.2925 (4)	0.3602 (3)	−0.0537 (4)	9.9 (3)	6.5 (4)	8.9 (3)	−0.8 (3)	4.7 (3)	0.6 (3)
O(1)	0.0825 (10)	0.4675 (9)	0.1271 (10)	11.0 (9)	9.4 (11)	11.1 (9)	−1.6 (8)	7.2 (8)	1.4 (7)
O(3)	0.1781 (11)	0.5818 (9)	−0.1076 (11)	10.2 (10)	9.7 (11)	9.4 (9)	2.3 (10)	3.9 (8)	2.3 (8)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
O(2)	0.1364 (8)	0.5843 (9)	0.0931 (8)	8.2 (3)	C(7)[a]	0.3823	0.5876	−0.1034	10.5 (12)
O(4)	0.3281 (11)	0.5274 (10)	−0.0456 (11)	10.9 (4)	C(8)[a]	0.3917	0.5310	−0.1913	11.1 (12)
O(5)	0.00	0.2293 (15)	0.25	11.9 (6)	C′(7)[a]	0.3355	0.5619	−0.1653	7.8 (14)
C(1)	0.1320 (15)	0.5063 (15)	0.0881 (15)	7.1 (6)	C′(8)[a]	0.4520	0.5549	−0.1250	10.7 (17)
C(2)	0.1983 (14)	0.4804 (13)	0.0202 (14)	6.8 (5)	C(9)[a]	−0.0996	0.1811	0.2032	11.0 (12)
C(3)	0.2285 (19)	0.5365 (17)	−0.0527 (18)	8.0 (7)	C(10)[a]	−0.1550	0.2173	0.0928	14.3 (19)
C(4)	0.2186 (12)	0.4068 (13)	0.0178 (11)	6.1 (5)	C′(9)[a]	−0.0688	0.1789	0.1450	10.4 (17)
C(5)	0.0697 (14)	0.6155 (13)	0.1567 (14)	8.6 (5)	C′(10)[a]	−0.1642	0.2249	0.1446	13.2 (25)
C(6)	0.0827 (17)	0.7011 (16)	0.1478 (17)	11.8 (7)					

b. Positional and Orientational[c] Parameters of Groups in $KCu(DED)_2{\cdot}OEt_2$

Group	x	y	z	ϕ	θ	ρ[d]	Atoms	% occupancy
ETH(2)	0.3870 (18)	0.5593 (21)	−0.1473 (24)	25.1 (40)	44.7 (25)	0.0	C(7), C(8)	60
ETH(2)	0.3938 (30)	0.5584 (27)	−0.1452 (33)	85.2 (38)	−18.8 (39)	0.0	C(7), C(8)	40
ETH(3)	−0.1273 (23)	0.1992 (22)	0.1480 (29)	−151.7 (54)	62.1 (35)	0.0	C(9), C(10)	60
ETH(3)	−0.1165 (36)	0.2019 (33)	0.1448 (38)	58.4 (35)	−0.2 (51)	0.0	C(9), C(10)	40

[a] Atomic positions generated from group coordinates. [b] In this table and Table III, the form of the temperature factor is $T = \exp[-0.25 \cdot (B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$ for anisotropic and $T = \exp[-B(\sin^2\theta)/\lambda^2]$ for isotropic thermal parameters. [c] Orientational parameters are given in degrees. [d] ρ must be fixed at an arbitrary value to allow refinement of the ethyl group. See text for definition of groups.

The least-squares program used minimizes $\sum w(\Delta|F|)^2$. The weighting function used throughout the refinement of both structures gives zero weight to those reflections with $F^2 \leq 3\sigma(F^2)$ and $w = 1/\sigma^2(F)$ to all others. The ignorance factor p in the expression for $\sigma^2(F^2)$ was 0.04 in both cases.[18]

The scattering factors of the neutral nonhydrogen atoms were taken from the tables of Doyle and Turner[19] and real and imaginary dispersion corrections[20] were applied to all of them. The spherical hydrogen scattering factor tables of Stewart, Davidson, and Simpson[21] were used in the refinement of the Ni structure.

$KCu(DED)_2{\cdot}O(C_2H_5)_2$.[22] Crystals suitable for x-ray diffraction work were obtained by crystallization from pyridine/ether mixtures. These were stable indefinitely at low temperatures (ca. −10 °C) but decomposed very slowly in air at room temperature.

A fresh crystal was mounted on a glass fiber in air and used for cell dimension measurements and data collection. The cell dimensions (Table I) were obtained by least-squares refinement on the 2θ values of 18 carefully centered reflections with 2θ between 24 and 28°.

A total of 1311 data were collected in the hemisphere of reciprocal space $\pm h,+k,\pm l$, with a basic scan width of 1.4° in 2θ. At $2\theta > 30°$ very few intensities were "observed" and data collection was halted.[23] Several reflections which had peak intensities greater than 10 000 counts/s were remeasured at the end of data collection with a zirconium attenuator placed in the diffracted beam and scaled by the known attenuation factor. The standard reflections showed an isotropic decline during the data collection period to 86% of their initial values and the data were corrected for this decay during processing.

Two reflections which had attenuated peak heights greater than 10 000 counts/s ((202), (110)) were eliminated from the final data set.

$(Me_3PhN)_2Ni(DED)_2$.[22] Crystals suitable for x-ray diffraction work were obtained on cooling a hot solution of the compound in nitromethane. A fragment of one of the needlelike crystals was mounted on a glass fiber in air and used for data collection and cell dimension determination.

The cell dimensions (Table I) were obtained by least-squares refinement on the setting angles of 12 carefully centered reflections with 2θ values between 25 and 30°.

A total of 2059 intensities were measured in the hemisphere of reciprocal space $+h,\pm k,\pm l$ out to a 2θ angle of 40° ($(\sin\theta)/\lambda \leq 0.481$), using a base width for the scan of 1.0° in 2θ. Zirconium attenuators were automatically inserted in the diffracted beam when the count rate exceeded 10 000 counts/s and the reflection and background counts were remeasured with the attenuators in place. The standard reflections showed no systematic variation over the data collection period.

Determination of the Structures

A. $KCu(DED)_2{\cdot}O(C_2H_5)_2$. A three-dimensional Patterson synthesis was solved in the centric space group $C2/c$ to yield the positions of the potassium, the copper, and the two sulfur atoms. The other nonhydrogen atoms were located on subsequent Fourier syntheses following least-squares refinements. These also revealed the ether molecule coordinated to the potassium. The refinement of all atoms with isotropic temperature factors gave a conventional R value of 0.11 but large thermal parameters and unreasonable distances for C(7) and C(8) in one of the ethyl groups of the DED ligand (ETH(2)) and C(9) and C(10) in the unique ethyl group of the ether molecule (ETH(3)). These two ethyl groups were then constrained to refine with a fixed C–C distance[24] of 1.54 Å and the copper, potassium, sulfur, and carbonyl oxygen atoms refined with anisotropic thermal parameters to an R_1 of 0.07. A difference Fourier showed broad peaks around the two constrained ethyl groups which suggested disorder. Several trial disorder schemes were refined with constraint on the ethyl C–C distance. A minimum R value was obtained for both ETH(2) and ETH(3) disordered with an occupation ratio of 60:40 for the two possible positions. The final R value was 0.060; the weighted R (Table I) was 0.068. During the last cycle of refinement all parameter shifts were less than 20% of their esd. No attempt was made to locate the hydrogen atoms, and the final difference Fourier map showed maximum deviations of +0.7 and −0.5 e/Å^3. The final parameters of the structure with their estimated standard deviations as calculated from the inverse least-squuares matrix are given in Table II.

B. $(Me_3PhN)_2Ni(DED)_2$. A three-dimensional Patterson synthesis yielded the positions of the nickel atom, at the origin, and of 17 other nonhydrogen atoms. Three cycles of least-squares refinement of the positions and isotropic thermal parameters of these atoms gave an R value of 0.32 and the subsequent Fourier synthesis revealed the remaining nonhydrogen atoms of the structure.

Refinement of all nonhydrogen atoms with anisotropic thermal parameters converged to an R_1 of 0.051. A difference Fourier showed peaks near the predicted positions for the hydrogen atoms, but many

Table III. Positional and Thermal Parameters of Atoms in $(Me_3PhN)_2Ni(DED)_2$

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0	0	0	3.53 (4)	3.41 (4)	3.92 (4)	1.45 (3)	1.57 (3)	−0.12 (3)
S(1)	0.1134 (2)	−0.1462 (1)	0.116 07 (8)	4.98 (7)	4.31 (7)	4.54 (6)	2.61 (6)	1.92 (5)	0.05 (5)
S(2)	−0.0547 (2)	0.0616 (2)	0.112 86 (8)	4.67 (7)	4.74 (7)	4.34 (6)	2.66 (5)	1.91 (5)	0.14 (5)
O(1)	0.2667 (5)	−0.2427 (5)	0.322 1 (2)	9.5 (3)	8.1 (2)	5.6 (2)	6.6 (2)	1.9 (2)	−0.3 (2)
O(2)	0.2343 (5)	−0.1426 (5)	0.435 2 (2)	8.2 (2)	7.3 (2)	4.2 (2)	5.0 (2)	2.0 (2)	0.8 (1)
O(3)	−0.0891 (6)	−0.0046 (5)	0.323 5 (3)	5.5 (2)	9.0 (3)	7.5 (2)	3.0 (2)	2.8 (2)	−1.3 (2)
O(4)	0.1903 (5)	0.1800 (5)	0.370 3 (3)	6.2 (2)	6.3 (2)	8.6 (2)	2.5 (2)	1.7 (2)	−3.4 (2)
C(1)	0.2115 (7)	−0.1569 (7)	0.344 7 (4)	5.1 (3)	5.4 (3)	4.0 (3)	2.5 (3)	1.0 (2)	−0.3 (2)
C(2)	0.1115 (6)	−0.0612 (5)	0.283 5 (3)	3.5 (2)	3.6 (2)	4.0 (3)	1.5 (2)	1.2 (2)	−0.6 (2)
C(3)	0.0565 (8)	0.0358 (7)	0.327 1 (3)	4.2 (3)	5.4 (3)	3.7 (2)	2.2 (3)	0.7 (2)	−0.3 (2)
C(4)	0.0650 (5)	−0.0539 (5)	0.187 7 (3)	3.1 (2)	2.8 (2)	4.5 (3)	0.7 (2)	1.7 (2)	−0.3 (2)
C(5)	0.3378 (10)	−0.2274 (9)	0.505 1 (5)	12.3 (5)	9.5 (5)	5.6 (4)	7.5 (4)	2.0 (3)	1.9 (3)
C(6)	0.3469 (12)	−0.1993 (12)	0.596 1 (5)	13.2 (6)	17.3 (8)	5.9 (4)	9.6 (6)	3.7 (4)	3.5 (4)
C(7)	0.1539 (11)	0.2844 (11)	0.418 7 (6)	12.1 (6)	12.2 (6)	9.9 (5)	6.9 (5)	1.3 (4)	−5.9 (4)
C(8)	0.2432 (14)	0.2818 (11)	0.517 4 (6)	19.8 (8)	12.2 (6)	8.0 (5)	10.3 (6)	7.9 (5)	2.0 (4)
N	0.4206 (5)	0.5766 (4)	0.151 8 (3)	3.5 (2)	3.4 (2)	6.1 (2)	1.2 (2)	1.5 (2)	−0.7 (2)
C(9)	0.5312 (6)	0.4814 (6)	0.160 7 (3)	3.9 (3)	3.1 (2)	5.1 (2)	1.3 (2)	1.9 (2)	−0.1 (2)
C(10)	0.4498 (7)	0.3138 (7)	0.136 9 (4)	4.3 (3)	4.4 (3)	9.7 (4)	1.6 (2)	2.9 (3)	−0.6 (3)
C(11)	0.5485 (9)	0.2238 (7)	0.145 2 (5)	6.9 (4)	4.5 (3)	11.4 (4)	2.5 (3)	4.1 (3)	−0.4 (3)
C(12)	0.7304 (9)	0.3021 (9)	0.180 6 (4)	7.3 (4)	6.8 (4)	7.1 (3)	4.8 (3)	4.0 (3)	1.9 (3)
C(13)	0.8097 (7)	0.4695 (8)	0.204 2 (4)	4.3 (3)	6.6 (4)	7.8 (3)	2.6 (3)	2.5 (2)	0.7 (3)
C(14)	0.7114 (7)	0.5607 (6)	0.194 8 (4)	3.8 (3)	4.6 (3)	7.7 (3)	1.7 (2)	2.0 (2)	0.1 (2)
C(15)	0.2701 (11)	0.5408 (11)	0.056 7 (5)	10.6 (5)	13.6 (6)	7.9 (4)	9.0 (5)	−1.2 (4)	−1.7 (4)
C(16)	0.3346 (11)	0.5096 (10)	0.221 5 (6)	12.5 (5)	12.0 (5)	11.8 (5)	7.3 (5)	7.8 (5)	1.0 (4)
C(17)	0.5196 (9)	0.7551 (8)	0.171 7 (10)	5.2 (4)	4.5 (4)	35.4 (14)	1.9 (3)	5.0 (5)	−3.8 (6)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(1)	0.0299	0.2416	0.4027	15.000	H(13)	0.7997	0.240	0.1877	10.000
H(2)	0.1933	0.3972	0.3992	15.000	H(14)	0.9354	0.5239	0.2278	10.000
H(3)	0.2189	0.3498	0.5482	15.000	H(15)	0.7678	0.6779	0.2117	10.000
H(4)	0.3673	0.3247	0.5336	15.000	H(16)	0.2014	0.6021	0.0522	20.000
H(5)	0.2039	0.1691	0.537	15.000	H(17)	0.1976	0.4235	0.0486	20.000
H(6)	0.454	−0.1834	0.5063	15.000	H(18)	0.3153	0.5742	0.0087	20.000
H(7)	0.2825	−0.345	0.4894	15.000	H(19)	0.2638	0.5686	0.2169	20.000
H(8)	0.4144	−0.2543	0.6426	15.000	H(20)	0.4238	0.5252	0.284	20.000
H(9)	0.2305	−0.2432	0.5946	15.000	H(21)	0.2620	0.3928	0.2076	20.000
H(10)	0.4020	−0.0816	0.6115	15.000	H(22)	0.4414	0.8072	0.1646	20.000
H(11)	0.3242	0.2595	0.1136	10.000	H(23)	0.5756	0.8013	0.1286	20.000
H(12)	0.4916	0.1069	0.1277	10.000	H(24)	0.607	0.775	0.2348	20.000

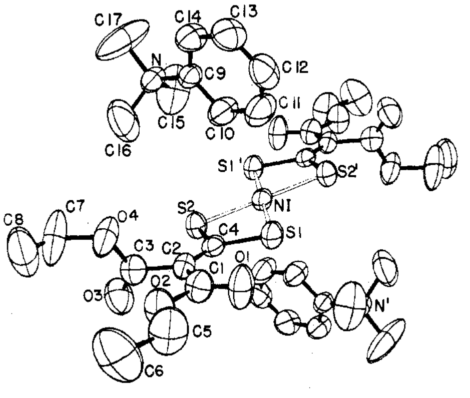

Figure 3. Molecular structure and labeling in $(Me_3PhN)_2Ni(DED)_2$. Thermal ellipsoids as drawn by ORTEP[43] represent the 50% probability surfaces. Primed atoms are related to unprimed atoms through the center of symmetry at the nickel atom. Hydrogen atoms have been omitted for clarity.

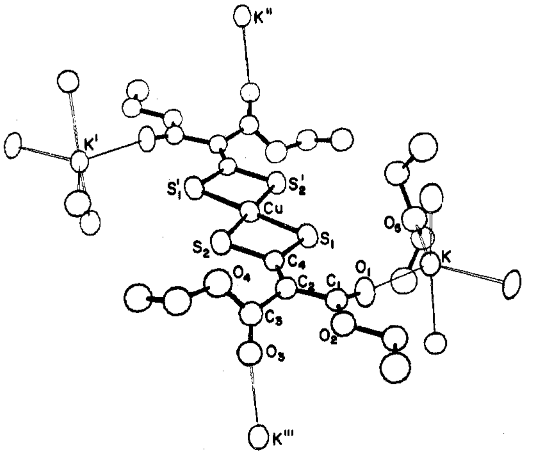

Figure 4. Molecular structure and labeling for $KCu(DED)_2 \cdot OEt_2$. The thermal ellipsoids as drawn by ORTEP[43] represent the 20% probability surfaces. Only the 60% occupied component of the disordered ethyl groups has been drawn.

were poorly resolved and the anisotropy of the motion of the carbon atoms of the ethyl groups of the ligand and the methyl groups of the cation suggested that refinement would not be feasible. Therefore, the idealized positions of the hydrogen atoms were calculated, using a carbon–hydrogen distance of 0.95 Å[26] and tetrahedral or planar geometry as required. The hydrogen atoms were included in calculation of the structure factors but not refined. The positions of the hydrogens were recalculated after each cycle of least squares, and their thermal parameters were held fixed at 15.0 Å^2 for the ethyl, 10.0 Å^2 for the phenyl, and 20.0 Å^2 for the methyl hydrogens.

Refinement converged to $R_1 = 0.038$, $R_2 = 0.053$. All parameter shifts in the last cycle were less than 5% of their estimated standard deviations. In the final difference Fourier map the highest peaks (~0.4 e/Å^3) were found in the region of the $N(CH_3)_3$ group, where the anisotropic thermal model gives the poorest fit. The final parameters and their esd's are given in Table III.

Listings of the observed structure factors, their esd's, and the differences ($|F_o| - |F_c|$) for both structures are available. (See paragraph at the end of the paper regarding supplementary material.)

Results and Discussion

In both structures (Figures 3 and 4), the central metal atom lies on a crystallographic center of symmetry which requires the MS_4 unit to be strictly planar. This plane forms a small

Table IV. Bond Distances (Å) and Angles (deg) in $(PhMe_3N)_2Ni(DED)_2$ and $KCu(DED)_2 \cdot O(C_2H_5)_2$

(a) Complex Anion

Distance	M = Ni	M = Cu	Angle	M = Ni	M = Cu
$M-S_1$	2.196 (1)	2.199 (5)	S_1-M-S_2	78.90 (6)	78.14 (24)
$M-S_2$	2.193 (1)	2.190 (5)	S_1-M-S_2'	101.10 (6)	101.87 (23)
$S_1 \cdots S_2$ (bite)	2.789 (2)	2.766 (6)	$M-S_1-C_4$	87.2 (2)	89.2 (6)
$S_1 \cdots S_2'$	3.389 (2)	3.407 (8)	$M-S_2-C_4$	87.1 (2)	89.6 (7)
C_4-S_1	1.738 (5)	1.77 (1)	$S_1-C_4-S_2$	106.2 (2)	102.9 (7)
C_4-S_2	1.749 (4)	1.76 (2)	$S_1-C_4-C_2$	129.2 (2)	128.6 (10)
C_4-C_2	1.367 (6)	1.32 (2)	$S_2-C_4-C_2$	124.6 (2)	128.5 (10)
C_2-C_1	1.450 (7)	1.51 (2)	$C_4-C_2-C_1$	124.5 (5)	118.3 (22)
C_2-C_3	1.486 (7)	1.50 (3)	$C_4-C_2-C_3$	117.7 (4)	121.6 (19)
C_1-O_1	1.208 (6)	1.18 (2)	$C_1-C_2-C_3$	118.4 (4)	119.6 (22)
C_1-O_2	1.348 (6)	1.37 (2)	$C_2-C_1-O_1$	127.6 (4)	127.0 (19)
C_3-O_3	1.190 (6)	1.15 (2)	$C_2-C_1-O_2$	110.5 (4)	107.5 (16)
C_3-O_4	1.337 (6)	1.36 (2)	$O_1-C_1-O_2$	121.9 (4)	125.5 (16)
O_2-C_5	1.449 (6)	1.50 (2)	$C_2-C_3-O_3$	125.5 (4)	127.5 (21)
C_5-C_6	1.430 (10)	1.52 (3)	$C_2-C_3-O_4$	112.0 (4)	110.0 (18)
O_4-C_7	1.465 (7)	1.60, 1.69[a]	$O_3-C_3-O_4$	122.5 (4)	122.4 (19)
C_7-C_8	1.404 (10)	1.54[b]	$C_1-O_2-C_5$	116.6 (5)	111.2 (22)
$S_1 \cdots O_1$	3.062 (4)	2.860 (15)	$O_2-C_5-C_6$	108.7 (4)	102.3 (14)
			$C_3-O_4-C_7$	117.2 (6)	119.6, 103.3[a]
			$O_4-C_7-C_8$	110.1 (5)	94.1, 90.1[a]

(b) Complex Cation

Distance		Distance		Angle		Angle	
$N-C_9$	1.498 (6)	$K-O_1$	2.610 (15)	C_9-N-C_{15}	110.5 (4)	$C_{12}-C_{13}-C_{14}$	121.1 (6)
$N-C_{15}$	1.491 (7)	$K-O_3$	2.647 (16)	C_9-N-C_{16}	108.3 (4)	$C_{13}-C_{14}-C_9$	119.2 (5)
$N-C_{16}$	1.507 (8)	$K-O_5$	2.784 (26)	C_9-N-C_{17}	114.1 (4)	O_5-K-O_1	122.2 (5)
$N-C_{17}$	1.437 (7)	$O_5 \cdots O_1$	4.723 (28)	$C_{15}-N-C_{16}$	105.1 (6)	O_5-K-O_3	101.4 (6)
C_9-C_{10}	1.357 (7)	$O_5 \cdots O_3$	4.205 (25)	$C_{15}-N-C_{17}$	111.0 (7)	O_1-K-O_3	80.5 (4)
$C_{10}-C_{11}$	1.372 (7)	$O_1 \cdots O_3$	3.397 (18)	$C_{16}-N-C_{17}$	107.4 (7)	O_1-K-O_3'	87.3 (5)
$C_{11}-C_{12}$	1.374 (8)	$O_1 \cdots O_3'$	3.630 (19)	$N-C_9-C_{10}$	119.1 (4)	O_1-K-O_1'	115.6 (4)
$C_{12}-C_{13}$	1.356 (8)	$O_1 \cdots O_1'$	4.417 (24)	$N-C_9-C_{14}$	120.5 (4)	O_3-K-O_3'	157.1 (10)
$C_{13}-C_{14}$	1.373 (7)	O_5-C_9	1.57, 1.66[a]	$C_{10}-C_9-C_{14}$	120.4 (5)	$K-O_5-C_9$	122.5, 122.1[a]
$C_{14}-C_9$	1.362 (6)	C_9-C_{10}	1.54[b]	$C_9-C_{10}-C_{11}$	120.1 (4)	$C_9-O_5-C_9'$	115.0, 115.7[a]
				$C_{10}-C_{11}-C_{12}$	120.0 (5)	$O_5-C_9-C_{10}$	105.8, 90.3[a]
				$C_{11}-C_{12}-C_{13}$	119.1 (6)		

[a] Distances and angles involving disordered ethyl groups refined as rigid bodies. The first and second entries refer to the groups having respectively 60% and 40% occupancy. Standard deviations are not available for these parameters. [b] Fixed by rigid-body refinement.

Table V. Deviations (Å) from Least-Squares Planes in $Ni(DED)_2^{2-}$ and $Cu(DED)_2^-$

Plane 1				Plane 2		Plane 3	
$Ni(DED)_2^{2-}$							
C(1)	0.010 (6)	S(2)	0.000 (1)	C(1)	−0.009 (6)	C(2)	0.002 (5)
C(2)	0.003 (5)	O(1)[a]	0.034 (5)	C(2)	0.002 (5)	C(3)	−0.009 (5)
C(3)	−0.024 (6)	O(2)[a]	0.020 (4)	O(1)	0.002 (5)	O(3)	0.002 (4)
C(4)	0.015 (5)	N[a]	−0.374 (4)	O(2)	0.001 (4)	O(4)	0.002 (4)
S(1)	−0.001 (1)	Ni[a]	−0.266[b]				
Dihedral angles: plane 1–plane 2, 0.7°; plane 1–plane 3, 77.7°; plane 1–NiS_4, 9.0°							
$Cu(DED)_2^-$							
C(1)	−0.050 (20)	S(2)	0.000 (1)	C(1)	−0.014 (20)	C(2)	−0.000 (20)
C(2)	−0.037 (18)	O(1)[a]	0.156 (13)	C(2)	0.003 (18)	C(3)	0.002 (25)
C(3)	0.131 (24)	O(2)[a]	−0.295 (11)	O(1)	0.002 (13)	O(3)	−0.000 (14)
C(4)	−0.025 (15)	K[a]	0.100[b]	O(2)	0.001 (11)	O(4)	−0.000 (15)
S(1)	−0.001 (1)	Cu[a]	0.193[b]				
Dihedral angles: plane 1–plane 2, 11.6°; plane 1–plane 3, 136.1°; plane 1–CuS_4, 6.5°							

[a] Atom not included in calculation of the best plant. [b] Due to symmetry restrictions no esd is available.

dihedral angle (9.0° for Ni, 6.5° for Cu) with the best plane (Table V) through the S_2C_4 "backbone" of the DED ligand. This "step" conformation has been observed in many sulfur chelates which contain a planar MS_4 group.[27-29] The two independent metal–sulfur distances in each of the two MS_4 groups are not significantly different from each other. In addition, the distances of the S···S intraligand ("bite") and interligand contacts (Table IV) are such that resonance forms involving disulfide bonds (Figure 2d, e) are not important in the description of the electronic structure of the copper complex. The DED ligands in the two structures are remarkably similar. In both structures one of the carboethoxy groups per ligand has been twisted around the C–C single bond so that it forms a large angle with the C_4S_2 "backbone" of the ligand. The other carboethoxy group is essentially coplanar with the "backbone" (Table V). The observed twisting confirms a prediction made earlier on the basis of infrared data from various DED complexes.[30]

A comparison of the bond distances in the DED ligands (Table IV) reveals a pattern of variation which would indicate

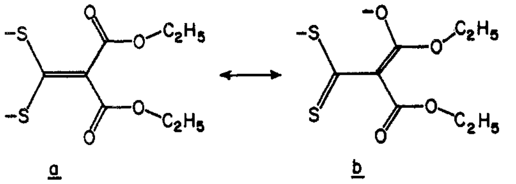

Figure 5. Resonance forms of the DED^{2-} ligand.

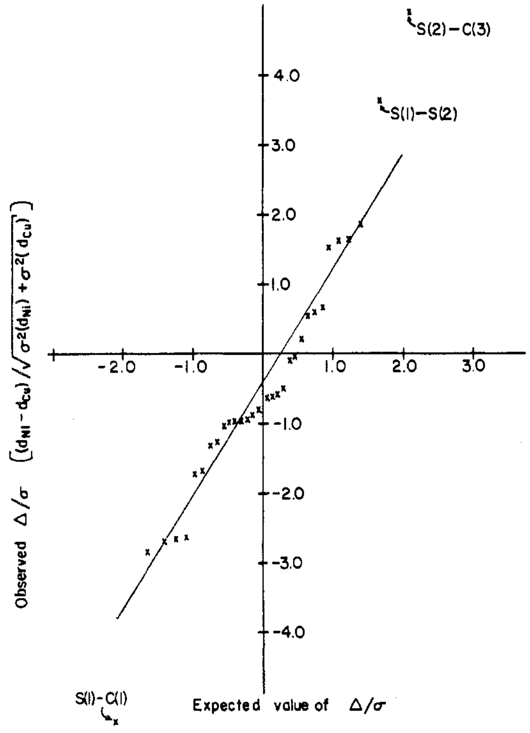

Figure 6. Normal probability plot comparing intraligand distances in the Ni(DED)$_2{}^{2-}$ and Cu(DED)$_2{}^{-}$ complexes. The least-squares line with slope 1.64 and intercept −0.45 (see text) is indicated.

that charge is more localized on the sulfur atoms in the Cu(III) complex than it is in the Ni(II) complex (i.e., the resonance form shown in Figure 5a is favored). However, the differences involved are all less than 3 times their combined standard deviation, $(\sigma_{\mathrm{Ni}}{}^2 + \sigma_{\mathrm{Cu}}{}^2)^{1/2}$, except for the difference in the S–S bite distance, which is 3.6 times its pooled esd. Little confidence could be placed, therefore, in conclusions based on the differences of individual bond lengths.

However, if the normalized differences, $(d_{\mathrm{Ni}} - d_{\mathrm{Cu}})/(\sigma^2(d_{\mathrm{Ni}}) + \sigma^2(d_{\mathrm{Cu}}))^{1/2}$, are ordered and plotted against the expected[31] values of a normal distribution of random errors, the resulting "normal probability plot" can act as an indicator of systematic differences affecting the ligand as a whole.[32,33] If there are no systematic effects present and the esd's have been assigned correctly, the plot should be linear with a slope of 1.0 and pass through the origin.

A normal probability plot of the differences $d_{\mathrm{Ni}} - d_{\mathrm{Cu}}$ for 34 intraligand distances involving bond lengths, bond angles, and torsion angles[32] was constructed. In this plot (Figure 6) distances involved in the torsion angles around C(1)–C(2) and C(2)–C(3) and all distances involving C(7) and C(8), which are disordered in the Cu(III) complex, were excluded. The plot is clearly nonlinear and intercepts the *y* axis well away from the origin, indicating that there are indeed systematic differences between the two ligands. The least-squares straight line through all of the points has a slope of 1.9, indicating a general underestimation of the esd's of the distances which is common in x-ray crystallographic studies.[32]

The extremes of the probability plot (labeled in Figure 6) represent differences in the configuration of the ligand around C(4) and C(2), in particular the angles S(2)–C(4)–C(2) and C(4)–C(2)–C(1) (vide infra). However, the remaining distances also show systematic deviation from a normal distribution (a least-squares line through the remaining points has a slope of 1.64 and an intercept of −0.45), and this deviation, taken as a whole, *is* significant. Analysis of the particular distances involved indicates that the nature of the systematic variation is precisely that expected, a reduction of resonance form b with respect to form a (Figure 5) in the copper complex. This change can be explained either by simple Coulombic arguments if a high positive charge is localized on the copper (i.e., Cu(III)) or by contributions from resonances forms of the type b and c, involving covalency of the Cu–S bond (Figure 2). The Ni–S distances lie in the middle of the range observed previously (2.13–2.24 Å).[27-29] The average Cu–S distance can be compared to the 2.22 (2) Å distance observed in $\mathrm{Cu}((n\text{-}\mathrm{Bu})_2\mathrm{dtc})_2\mathrm{I}_3$[12,34] and the 2.19 (1) Å distance in $\mathrm{CuBr}_2((n\text{-}\mathrm{Bu})_2\mathrm{dtc})$[35] where the copper atom is chelated by the 1,1-dithio acid moiety in oxidized planar complexes.

The potassium ion is five-coordinate, and the coordination geometry can best be described as distorted trigonal bipyramidal with the two O(1) carbonyl oxygens and the ether oxygen defining the equatorial plane (Figure 7, Table IV). Although 5 is a low coordination number for potassium, it can be seen from Figure 7 that while S(1) is too far away (3.824 (5) Å) to be considered a coordinating atom, it does occupy a possible coordination site and blocks further coordination. The low coordination number must be considered a consequence of the efficient packing of the structure.

The strong interaction of the potassium ions also accounts for the deviation in the angles around C(4) and C(2) mentioned above, overcoming the repulsion of the essentially coplanar thiolate and carbonyl groups and reducing the S(1)···O(1) distance from 3.06 Å in the Ni(II) complex to 2.86 Å in the Cu(III) complex.

Intramolecular contacts are normal between both the anions themselves and the ether of solvation. There are only three nonbonded contacts less than 3.5 Å. They are between O(1) and C(1) of neighboring layers (3.42 (2) Å), between O(3)

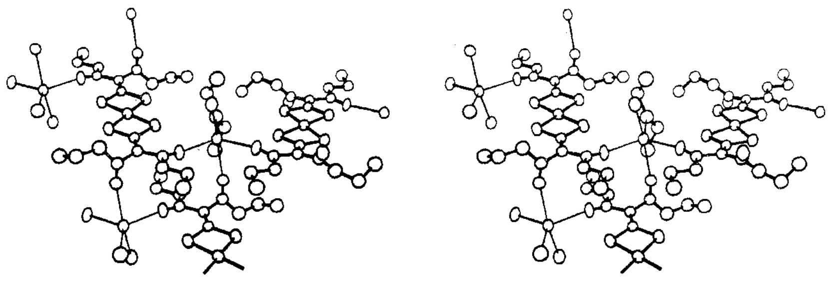

Figure 7. Stereoscopic view of the packing in KCu(DED)$_2$·OEt$_2$ showing the linkage of the anions into a three-dimensional structure by the potassium coordination. Only the 60% occupied component of the disordered ethyl groups is shown.

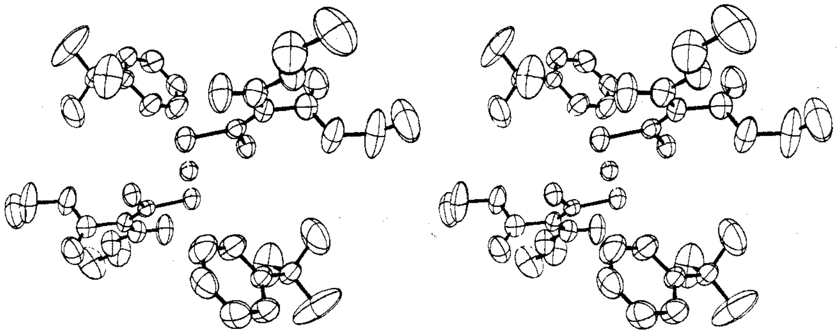

Figure 8. Stereoscopic view of the contents of one unit cell of $(Me_3PhN)_2Ni(DED)_2$ as drawn by ORTEP.[43] This view is from the same direction and with the same thermal ellipsoids as Figure 3.

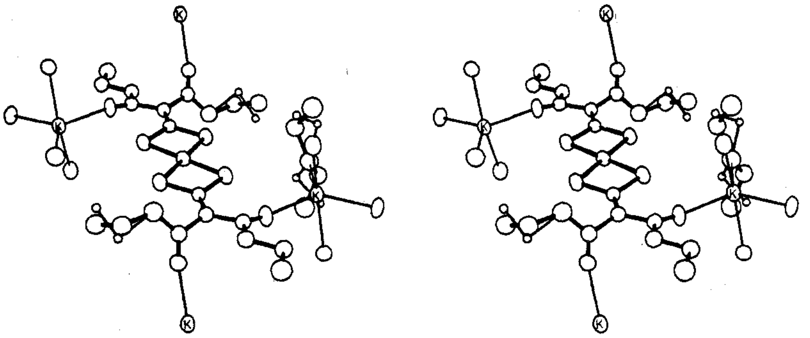

Figure 9. Stereoscopic view of the molecular structure of $KCu(DED)_2 \cdot OEt_2$, illustrating the disordered ethyl groups on the ligand and the ether. Thermal ellipsoids are drawn at the 20% probability surface for the ordered atoms and for the 60% occupancy atoms. The atoms with occupancy of 40% are represented by arbitrary small spheres.

and C(10) of the 40% occupied ether (3.42 (2) Å), and between C(7) of the 60% occupied ETH(2) and C(9) of the 40% occupied ether molecule (3.47 (2) Å) (Figure 7).

The packing of the Ni(II) complex is shown in Figure 8. The plane of the phenyl ring makes an angle of 86.6° with the NiS_4 plane. All contact distances between the cation and the anion are normal, as are all bond distances within the cation itself (Table IV).

The packing of the anions and cations for the Cu(III) complex is shown in Figures 7 and 9 and illustrates the nature of the disorder in the structure. The potassium ions lie on a crystallographic twofold axis and link the complex anions into infinite ribbons through coordination by carbonyl oxygen O(1), approximately in the plane of the ligand (the potassium ion lies only 0.1 Å from the mean plane through the ligand backbone). The potassium then links these ribbons together into an infinite three-dimensional structure through coordination by the second carbonyl oxygen, O(3). The coordination sphere of the potassium is completed by the oxygen of the ether molecule, which occupies holes in the three-dimensional cation–anion structure.

M–S Bonding. A description of the M–S bonding in highly oxidized sulfur chelates presents a problem when the relative importance of ionic vs. covalent character is to be considered. An ionic bond can be envisioned if the oxidation is centered on the metal ion (Figure 2a), while a covalent bond results when a mercaptide free-radical electron is coupled with a metal d electron (Figure 2c).

The identical Ni–S and Cu–S bond distances observed in the structures reported herein (2.194 (5) Å) can be rationalized in terms of either the ionic or covalent models. In the structure of the $Cu(DED)_2^{2-}$ complex, values of the ligand structural parameters when taken individually do not seem to be significantly different from those in the Ni(II) complex at the 3σ level. However, the probability plot (Figure 6) shows that, collectively, the ligand parameters in the copper complex are systematically different from those in the nickel complex.

The observed differences are consistent with a greater localization of charge on the sulfur atoms of the DED ligand in the copper complex. This localization can be envisioned as a consequence of Coulombic effects due to a Cu(III) ion. This interpretation of the data must take into account the following observations: (a) the expected reduction of the ionic radius of copper is not reflected in a shorter Cu–S bond and (b) the slightly greater contribution of form a (Figure 5) to the structure of the ligand is not evident in the frequencies of the C–O vibrations in the copper complex. The first of the two observations can be rationalized if a concomitant increase of the ionic radii of the sulfur donors offsets the effect of a shorter Cu(III) radius. The similar C–O vibrations at 1712 and 1683 cm^{-1} for the copper complex and 1713 and 1678 cm^{-1} for the nickel complex[36] can be explained if the C═O vibration is strongly coupled with the C—C vibration.

The identical lengths of the Ni–S and Cu–S bonds also can be interpreted in terms of significant covalency in the Cu–S bond. Recently, similar Fe–S bond lengths in the *low-spin* $Fe(pyrr(dtc))_3^+$ and $Fe(Et_2dtc)_3$ complexes[8] (2.300 (2) and 2.306 (1) Å, respectively) led investigators to the conclusion that an increase of the oxidation state of iron had only a minimal contribution to a shortening of the Fe–S bond.[8a]

Arguments for covalency in the M–S bond of oxidized sulfur chelates also can be advanced by a study of redox potentials. Particularly in copper complexes, the nature of the ligands seems to affect the ease of reduction of the oxidized copper chelates. The reduction potentials of the copper(III) tetrapeptide complexes[37] (0.60 and 0.58 V, respectively, for the tetraglycine and tetraalanine complexes of Cu(III)) are at the high end of the observed range, and these molecules will oxidize iodide ions. Somewhat lower values are observed[38] with various "Cu(III)" sulfur chelates (0.47–0.19 V) and these often are obtained by I_2 oxidation of the reduced complexes. Finally the $Cu(DED)_2^-$ complex reduces with great difficulty (−0.50 V) and the $Cu(DED)_2^{2-}$ complex is oxidized readily by air in water solution.[36]

The degree of covalency in the Cu–N bond of oxidized nitrogen chelates probably is minimal; however, the lower values and variations in the redox potentials of sulfur chelates suggest that various degrees of covalency in the Cu–S bonds are important. It is apparent that a convincing case cannot be made for either an ionic or a covalent description of the M–S bond in oxidized sulfur chelates. The oxidation of sulfur chelates perhaps can be described better as a loss of electron(s) from an orbital composed primarily of metal and sulfur atomic functions. The relative contribution of sulfur atomic functions to this molecular orbital will depend on the electronic characteristics of the sulfur ligands under consideration.

A description which attributes oxidation of metal–sulfur complexes to electron loss from the M–S bond may be applicable to certain biological systems. The coordination environment of an M–S chromophore then would be of importance in determining the potential of electron transfer. In galactose oxidase, M–S coordination is implicated[39] and the presence of Cu(III) has been proposed for the metal ion in the active state of the enzyme.[40] The presence of the $\mathrm{Cu^{III}}$–S chromophore in the active form of galactose oxidase may be one of several other thiometallyl groups in biological systems capable of undergoing a two-electron-transfer reaction of the type

$$\text{thiometallyl}^{n+} \underset{-2e^-}{\overset{+2e^-}{\rightleftharpoons}} \text{thiometallyl}^{(n-2)+}$$

Although the axial ligands in horseradish peroxidase[41] are not known with certainty, the possibility exists that the $\mathrm{Fe^{IV}}$–S chromophore is present in the two oxidized forms (compounds I and II, respectively), for which Mössbauer data show the presence of what formally has been described as Fe(IV).[42]

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Supplementary Material Available: Listings of observed structure factor amplitudes, their estimated standard deviations and the difference $|F_o| - |F_c|$ (13 pages). Ordering information is given on any current masthead page.

References and Notes

(1) J. A. McCleverty, *Prog. Inorg. Chem.*, **10**, 49 (1968).

(2) A. Davison, N. Edelstein, R. H. Holm, and H. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963).

(3) D. Coucouvanis, *Prog. Inorg. Chem.*, **11**, 233 (1970).

(4) D. Coucouvanis and J. P. Fackler, *J. Am. Chem. Soc.*, **89**, 1346 (1967).

(5) D. Coucouvanis and S. J. Lippard, *J. Am. Chem. Soc.*, **90**, 3281 (1968).

(6) A. R. Hendrickson, R. L. Martin, and N. M. Rohde, *Inorg. Chem.*, **14**, 1894 (1975), and references therein.

(7) E. A. Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).

(8) (a) R. L. Martin, N. M. Rohde, G. B. Robertson, and D. Taylor, *J. Am. Chem. Soc.*, **96**, 3647 (1974); (b) J. G. Leipoldt and P. Coppens, *Inorg. Chem.*, **12**, 2269 (1973).

(9) K. L. Brown, *Cryst. Struct. Commun.*, **3**, 493 (1974).

(10) A. Avdeef, J. P. Fackler, and R. G. Fischer, *J. Am. Chem. Soc.*, **92**, 6972 (1970).

(11) H. C. Brinkhoff, Ph.D. Thesis, The University of Nijmegen, 1970.

(12) J. G. Wijnhoven, T. E. M. van den Hark, and P. T. Beurskens, *J. Cryst. Mol. Struct.*, **2**, 189 (1972).

(13) B. L. Edgar, D. J. Duffy, M. C. Palazzotto, and L. H. Pignolet, *J. Am. Chem. Soc.*, **95**, 1125 (1973).

(14) (a) F. J. Hollander, M. L. Caffery, and D. Coucouvanis, *J. Am. Chem. Soc.*, **96**, 4682 (1974); (b) F. J. Hollander, R. Pedelty, and D. Coucouvanis, *ibid.*, **96**, 4032 (1974).

(15) J. A. Fee, *Struct. Bonding* (*Berlin*), **23**, 1 (1975).

(16) H. Beinert in "The Biochemistry of Copper", J. Peisach, P. Aisen, and W. E. Blumberg, Ed., Academic Press, New York, N.Y., 1966, p 213.

(17) P. Hemmerich in "The Biochemistry of Copper", J. Peisach, P. Aisen, and W. E. Blumberg, Ed., Academic Press, New York, N.Y., 1966, p 15.

(18) A complete description of the data reduction procedures has been given previously: F. J. Hollander and D. Coucouvanis, *Inorg. Chem.*, **13**, 2381 (1974).

(19) P. A. Doyle and P. S. Turner, *Acta Crystallogr., Sect. A*, **24**, 390 (1968).

(20) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(21) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(22) The synthesis of these complexes will be published: D. Coucouvanis, M. L. Caffery, and R. Pedelty, paper in preparation.

(23) This 2θ value corresponds to a resolution of 1.4 Å. Despite extensive search, no better crystal could be obtained for crystallographic work.

(24) The origin of the group coordinate system was taken midway between the two carbon atoms, which were chosen to lie on the y axis. With this choice of coordinate system the angle ρ as defined by Scheringer[25] must be held fixed.[18]

(25) C. Scheringer, *Acta Crystallogr.*, **16**, 546 (1963).

(26) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

(27) D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, *Inorg. Chem.*, **13**, 1191 (1974).

(28) R. H. Holm and M. J. O'Conner, *Prog. Inorg. Chem.*, **14**, 241 (1972).

(29) D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, *J. Am. Chem. Soc.*, **95**, 3875 (1973).

(30) K. A. Jensen and L. Henriksen, *Acta Chem. Scand.*, **22**, 1107 (1968).

(31) W. C. Hamilton and S. C. Abrahams, *Acta Crystallogr., Sect. A*, **28**, 215 (1972).

(32) W. H. DeCamp, *Acta Crystallogr., Sect. A*, **29**, 148 (1973).

(33) S. C. Abrahams and E. T. Keve, *Acta Crystallogr., Sect. A*, **27**, 157 (1971).

(34) $(n\text{-Bu})_2\text{dtc}$ = di-*n*-butyldithiocarbamate anion.

(35) P. T. Beurskens, J. A. Cras, and J. J. Steggerda, *Inorg. Chem.*, **7**, 810 (1968).

(36) M. L. Caffery, Ph.D. Thesis, University of Iowa, 1973. The potentials were obtained in CH_2Cl_2 vs. Ag/AgI with Bu_4NClO_4 as the supporting electrolyte.

(37) D. W. Margerum, K. L. Chellappa, F. P. Bossu, and G. L. Burce, *J. Am. Chem. Soc.*, **97**, 6894 (1975).

(38) J. G. M. van der Linden, Ph.D. Thesis, University of Nijmegen, 1972. The values of reported potentials are from measurements in CH_2Cl_2 vs. SCE.

(39) L. Cleveland, R. E. Coffman, P. Coon, and L. Davis, *Biochemistry*, **14**, 1108 (1975).

(40) G. A. Hamilton, R. D. Libby, and C. R. Hartzell, *Biochem. Biophys. Res. Commun.*, **55**, 333 (1973).

(41) T. H. Moss, H. Ehrenberg, and A. J. Bearden, *Biochemistry*, **8**, 4519 (1969).

(42) B. C. Saunders, *Inorg. Biochem.*, 988 (1973).

(43) C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.