(4) V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta, and G. S. Laurence, *Coord. Chem. Rev.*, **15**, 321 (1975).
(5) G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 2337 (1976), and references therein.
(6) C. T. Lin, W. Bottcher, M. Chou, C. Creutz, and N. Sutin, *J. Am. Chem. Soc.*, **98**, 6536 (1976), and references therein.
(7) A. Juris, M. T. Gandolfi, M. F. Manfrin, and V. Balzani, *J. Am. Chem. Soc.*, **98**, 1047 (1976), and references therein.
(8) G. A. Crosby, R. J. Watts, and D. H. W. Carstens, *Science*, **170**, 1195 (1970).
(9) M. K. DeArmond and J. E. Hillis, *J. Chem. Phys.*, **54**, 2247 (1971).
(10) R. J. Watts and G. A. Crosby, *Chem. Phys. Lett.*, **13**, 619 (1972).
(11) G. A. Crosby, K. W. Hipps, and W. H. Elfring, Jr., *J. Am. Chem. Soc.*, **96**, 629 (1974).
(12) C. M. Flynn, Jr., and J. N. Demas, *J. Am. Chem. Soc.*, **96**, 1959 (1974).
(13) J. N. Demas, E. W. Harris, C. M. Flynn, Jr., and D. Diemante, *J. Am. Chem. Soc.*, **97**, 3838 (1975).
(14) B. Martin and G. M. Waind, *J. Chem. Soc.*, 4284 (1958).
(15) B. Martin, W. R. McWinnie, and G. M. Waind, *J. Inorg. Nucl. Chem.*, **23**, 207 (1961).
(16) B. Chiswell and S. E. Livingstone, *J. Inorg. Nucl. Chem.*, **26**, 47 (1964).
(17) K. R. Wunschel, Jr., and W. E. Ohnesorge, *J. Am. Chem. Soc.*, **89**, 2777 (1967).
(18) G. A. Crosby and D. H. W. Carstens, "Molecular Luminescence", E. C. Linn, ed., W. A. Benjamin, New York, N.Y., 1969, p 309.
(19) R. D. Gillard and B. T. Heaton, *J. Chem. Soc. A*, 451 (1969).
(20) J. A. Broomhead and W. Grumley, *J. Inorg. Nucl. Chem.*, **29**, 2126 (1967).
(21) L. H. Berka, R. R. Gagne, G. E. Philippon, and C. E. Wheeler, *Inorg. Chem.*, **9**, 2705 (1970).
(22) J. A. Broomhead and W. Grumley, *Inorg. Chem.*, **10**, 2002 (1971).
(23) R. J. Watts and J. S. Harrington, *J. Inorg. Nucl. Chem.*, **37**, 1293 (1973).
(24) J. N. Demas and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 2841 (1971).
(25) R. J. Watts and G. A. Crosby, *J. Am. Chem. Soc.*, **93**, 3184 (1971); R. J. Watts and G. A. Crosby, *ibid.*, **94**, 2606 (1972).
(26) R. J. Watts, G. A. Crosby, and J. L. Sansregrett, *Inorg. Chem.*, **11**, 1474 (1972).
(27) J. E. Hillis and M. K. DeArmond, *J. Lumin.*, **4**, 273 (1971).
(28) R. Ballardini, G. Varani, L. Moggi, and V. Balzani, *J. Am. Chem. Soc.*, **96**, 7123 (1974).
(29) R. Ballardini, G. Varani, L. Moggi, V. Balzani, K. R. Olson, F. Scandola, and M. Z. Hoffman, *J. Am. Chem. Soc.*, **97**, 728 (1975).
(30) R. J. Watts, T. P. White, and B. G. Griffith, *J. Am. Chem. Soc.*, **97**, 6914 (1975).
(31) R. J. Watts, *J. Am. Chem. Soc.*, **96**, 6186 (1974).
(32) R. J. Watts, M. Brown, B. G. Griffith, and J. S. Harrington, *J. Am. Chem. Soc.*, **97**, 6029 (1975).
(33) R. J. Watts, B. J. Griffith, and J. S. Harrington, *J. Am. Chem. Soc.*, **98**, 674 (1976).
(34) J. A. Broomhead and W. Grumley, *Chem. Commun.*, 1211 (1968).
(35) L. H. Berka and G. E. Philippon, *J. Inorg. Nucl. Chem.*, **32**, 3355 (1970).
(36) M. M. Muir and W.-L. Huang, *Inorg. Chem.*, 12, 1930 (1973).
(37) M. Kasha, *Discuss. Faraday Soc.*, **9**, 14 (1950).
(38) S. P. McGlynn, T. Azumi, and M. Kinoshida, "Molecular Spectroscopy of the Triplet State", Prentice-Hall, Englewood Cliffs, N.J., 1969, p. 7.
(39) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York, N.Y., 1971.
(40) The slight difference between the elemental analyses of samples A and B of Ir(Me$_2$phen)$_2$Cl$_2^+$ may correspond to the presence of five (instead of three) water molecules in sample A.
(41) In spite of considerable efforts by several laboratories, no *trans*-M(phen)$_2$X$_2$ complex has yet been obtained. See, for example, M. P. Hancock, J. Josephsen, and C. E. Schäffer, *Acta Chem. Scand., Ser. A*, **30**, 79 (1976).
(42) Another reason for discarding the aquo products is that their luminescence emission is weaker than that of the Ir(AA)$_2$Cl$_2^+$ complexes.
(43) A reddish compound which exhibits an emission band around 500 nm is also produced by heating phenanthroline alone in glycerol at 290 °C. This compound was found to behave as the complexes during the chromatographic elution.

Absence of Metal Interaction with Sulfur in Two Metal Complexes of a Cysteine Derivative. The Structural Characterization of Bis(*S*-methyl-L-cysteinato)cadmium(II) and Bis(*S*-methyl-L-cysteinato)zinc(II)

Patrice de Meester and Derek J. Hodgson*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514.

Received February 16, 1977

Abstract: The complexes bis(*S*-methyl-L-cysteinato)cadmium(II) (Cd(SMC)$_2$, C$_8$H$_{16}$CdN$_2$O$_4$S$_2$) and bis(*S*-methyl-L-cysteinato)zinc(II) (Zn(SMC)$_2$, C$_8$H$_{16}$ZnN$_2$O$_4$S$_2$) have been synthesized and their crystal structures have been determined from three-dimensional single-crystal x-ray counter data. The complex Cd(SMC)$_2$ crystallizes in the monoclinic space group $P2_1$ with two formula units in a cell of dimensions a = 13.314 (9), b = 5.074 (4), c = 9.839 (7) Å and β = 96.34 (4)°. Full-matrix least-squares refinement has reached an R factor (on F) of 0.052 for 913 independent reflections with $F^2 > 2\sigma(F^2)$. The complex is a polymer extending approximately in the crystallographic b-c plane. Two SMC ligands coordinate to the cadmium atom through N(amino) and O(carboxylate) with bonds ranging from 2.26 (1) to 2.28 (2) Å. The slightly distorted octahedral geometry at the metal atom is completed by two carboxylate oxygen atoms of neighboring ligands, at longer distances Cd-O of 2.46 (1) and 2.47 (2) Å. This complex has a structure very similar to that of bis(L-methioninato)cadmium(II). The complex Zn(SMC)$_2$ is also monoclinic, space group $P2_1$ with a cell of dimensions a = 13.433 (12), b = 5.323 (4), c = 9.603 (8) Å and β = 107.52 (3)° with two formula units per cell. Full-matrix least-squares refinement has reached R = 0.059 (on F) using 1330 independent reflections with $F^2 > 2\sigma(F^2)$. The Zn(SMC)$_2$ complex, which is not isostructural with Cd(SMC)$_2$, consists of infinite chains centered about a twofold screw axis parallel to b. The zinc atoms have the less usual trigonal-bipyramidal geometry with three Zn-O(carboxylate) bonds [1.980 (7) to 2.125 (6) Å] and two Zn-N(amino) bonds of 2.035 (7) and 2.087 (9) Å. One of the two SMC ligands coordinates to the metal via its two carboxylate oxygen atoms and its amino nitrogen atom, while the other SMC ligand donates only one carboxylate oxygen atom and its amino nitrogen atom.

Introduction

The role of sulfur-containing ligands, such as BAL (2,3-dimercaptopropanol),[1] 2,3-dimercaptosuccinic acid,[2] and derivatives of cysteine like penicillamine (β,β-dimethylcysteine) and N-acetylpenicillamine, is currently being investigated in several laboratories in order to have a better understanding of their potential therapeutic action against toxic heavy metal ions.[3-6] A definite body of single-crystal determinations of such metal complexes is now available and has led to more direct information concerning the nature and extent of metal bonding. Cysteine or its derivatives present three

Table I. Crystal Data for $Cd(SMC)_2$

$C_8H_{16}O_4N_2S_2Cd$
Crystal system: monoclinic
Space group: $P2_1$
a = 13.314 (8) Å
b = 5.074 (4) Å
c = 9.839 (7) Å
β = 96.34 (4)°
V = 660.6 Å^3
Z = 2
Mol wt: 380.8
d_m: 1.89 (2) g cm^{-3}
d_c: 1.914 g cm^{-3}
Radiation: Mo Kα
Graphite monochromator
Crystal orientation: ca. 0.8° from [010]
Take-off angle: 1.8°
Maximum 2θ: 50°
Scan type: θ–2θ
Scan speed: 0.5°/min
Scan range: $\Delta(2\theta) = (1.80 + 0.692 \tan\theta)°$, starting the scan from −0.90° below the calculated Kα_1 peak position
Background measurements: stationary-counter, stationary-crystal background counts of 40 s at each end of the scan
Number of independent reflections used, with $I > 2\sigma(I)$: 913
Standard reflections: three remeasured after every 99 reflections at the end of data collection, (300), (102), and (011) decreased by ca. 13, 12, and 9%, respectively. The decay was nonlinear, and no correction for decay was applied
Absorption coefficient: μ(Mo Kα). 19.5 cm^{-1}
Transmission coefficients range: 0.866 to 0.980
Crystal faces: (010), $(0\bar{1}0)$, (100), $(\bar{1}00)$, (001) and $(00\bar{1})$
Crystal dimensions: 0.77 × 0.08 × 0.01 mm

Table II. Crystal Data for $Zn(SMC)_2$

$C_8H_{16}O_4N_2S_2Zn$
Crystal system: monoclinic
Space group: $P2_1$
a = 13.433 (12) Å
b = 5.323 (4) Å
c = 9.603 (8) Å
β = 107.52 (3)°
V = 654.8 Å^3
Z = 2
Mol wt: 333.7
d_m: 1.67 (3) g cm^{-3}
d_c: 1.693 g cm^{-3}
Radiation: Mo Kα
Graphite monochromator
Crystal orientation: ca. 0.6° from [010]
Take-off angle: 1.9°
Maximum 2θ: 55°
Scan type: θ–2θ
Scan speed: 1°/min
Scan range: $\Delta(2\theta) = (2.80 + 0.692 \tan\theta)°$, starting the scan from −1.40° below the calculated Kα_1 peak position
Background measurements: stationary-counter, stationary-crystal background counts of 40 s at each end of the scan
Number of reflections used, with $I > 2\sigma(I)$: 1330
Standard reflections: 4 remeasured after every 99 reflections. At the end of data collection, (004) and $(00\bar{4})$ decreased by ca. 20% and $(60\bar{1})$ and $(\bar{6}01)$ by ca. 22%. The decay was nonlinear, and no correction for decay was applied.
Absorption coefficient: μ(Mo Kα) = 22.4 cm^{-1}
Transmission coefficients range: 0.728 to 0.881
Crystal faces: (100), $(\bar{1}00)$, $(0\bar{1}0)$, $(00\bar{1})$, $(\bar{1}01)$, $(\bar{1}22)$, and $(12\bar{2})$.
Crystal dimensions: 0.80 × 0.12 × 0.06 mm

potential coordination sites for metal bonding: S, N, and O. All three sites have been found to participate in metal bonding in Pb^{II}(D-pen)[7] (pen = penicillamine), Cd^{II}(D-pen),[8] $[Co^{III}(SMC)]^+$[9] (SMC = *S*-methyl-L-cysteine), $[Co^{III}(D,L\text{-pen})_2]^-$,[10] Co^{III}(L-his)(D-pen)[11,12] (his = histidyl), Cr^{III}(L-his)(D-pen),[11,13] $[Co^{III}{}_2$(L-his)(D-pen)(D-his)(L-pen),[11] $[Cr^{III}(L\text{-cys})]^-$[14] (cys = cysteinato), and $[Mo^V{}_2O_4(L\text{-cys})_2]^{2-}$.[15] Only the sites S and N are involved in $Cu^I{}_8Cu^{II}{}_6(D\text{-pen})_{12}$,[16] in $Pd^{II}(SMC)Cl_2$,[17] in four complexes of Mo[18–20] with L-cys or its methyl or ethyl esters, and in $(CH_3Hg)_2$(DL-pen),[21] but in Cd^{II}(DL-pen)Br[22] it has been found that S and O are the only sites of metal bonding. In four complexes of L-cysteine[23] or DL-pen[24,25] with Hg(II) or methylmercury(II), only the sulfur atom interacts with the metal. In all metal complexes with cysteine or its derivatives, the sulfur has been found to coordinate to the metal.

In metal complexes of met (met = methionine), which is identical with SMC except for an extra CH_2 group between S and C$^\alpha$, metal bonding occurs at S and N in $Pt^{II}(L\text{-met})Cl_2$,[26] Pt^{II}(gly-L-met)Cl,[26] and $Pd^{II}(met)Cl_2$,[27] at S and O in $[Hg^{II}(met)_2]^{2+}$,[24] and at N and O in $Cu(DL\text{-met})_2$,[28] $Cd^{II}(L\text{-met})_2$,[29] and $Zn^{II}(L\text{-met})_2$.[30] Since met does not bind to the metal via S in these three last complexes, possibly because of ring size (the metal coordination through S and O would involve a seven membered ring), we thought it important to study Cd(II) and Zn(II) complexes with SMC, a ligand potentially more favorable for tridentate coordination than met.

We report here the preparation and structural characterization of $Cd^{II}(SMC)_2$ and $Zn^{II}(SMC)_2$.

Experimental Section

Preparation and Data Collection. Bis(*S*-methyl-L-cysteinato)cadmium(II), $Cd(SMC)_2$, was prepared by adding 1 mmol of cadmium chloride dissolved in 5 mL of water to 2 mmol of *S*-methyl-L-cysteine dissolved in 20 mL of water. The pH was adjusted to a little below 7 by addition of diluted NaOH. Bis(*S*-methyl-L-cysteinato)zinc(II), $Zn(Smc)_2$, was prepared in a similar manner, using 1 mmol of zinc perchlorate and 1 mmol of *S*-methyl-L-cysteine. Colorless crystals of both complexes appeared after about 2 days, those of $Cd(SMC)_2$ being very thin plate-like needles, while those of $Zn(SMC)_2$ were much larger. Preliminary Weissenberg and precession photographs showed that the two complexes belonged to the monoclinic space group $P2_1$. Accurate cell constants were obtained by least-squares methods.[31] The pertinent crystal data for $Cd(SMC)_2$ and $Zn(SMC)_2$ are listed in Tables I and II, respectively. Both data sets were processed by the procedure of Ibers and co-workers[32] and corrected for Lorentz and polarization effects and for absorption.[33]

Solution and Refinement. Both structures were solved by standard Patterson and difference Fourier methods. All least-squares refinements in this work were on F, the function minimized being $\Sigma w(F_o - F_c)^2$ where the weights w were taken as $4|F_o|^2/\sigma^2(F_o{}^2)$. In calculations of F_c, the atomic scattering factors for nonhydrogen atoms were taken from "International Tables for X-ray Crystallography", Vol. IV,[34] and those for H from Stewart, Davidson, and Simpson.[35] The effects of the anomalous dispersion for Cd (or Zn) and S were taken into account in calculations of F_c: the values of $\Delta f'$ and $\Delta f''$ were also taken from "International Tables for X-ray Crystallography".[34] The conventional R factors used in the least-squares refinement are: $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(|F_o|)^2]^{1/2}$.

$Cd(SMC)_2$. Full-matrix isotropic least-squares refinement on the position of the cadmium atom alone, deduced from the Patterson function, led to R_1 = 0.319 and R_2 = 0.374. Successive difference Fourier maps revealed the positions of all remaining nonhydrogen atoms. Subsequent refinement with Cd and all S atoms anisotropic and all nonhydrogen atoms isotropic reduced R_1 and R_2 to 0.057 and 0.059, respectively. After making certain that these atomic positions were consistent with the presence of the L isomer of the ligand in the complex, an attempt was made to refine all atoms anisotropically. Although R_1 and R_2 decreased to the same value of 0.047, the carboxylate oxygen atom O(1) had nonpositive components of its thermal ellipsoid. Moreover, a calculation of bond lengths and angles at this stage did not show any significant improvement compared to the values obtained in the previous refinement. Since the crystals suffered decomposition during data collection (see Table I), and the decay was nonlinear (for this reason no correction for decay was applied), it was felt that anisotropic refinement of only the cadmium and sulfur atoms was justified. On this basis, a difference Fourier map was calculated which showed the position of 11 of the hydrogen atoms. The remaining hydrogen atoms were calculated on the assumption of tetrahedral geometry at both C and N atoms and C–H and N–H bond distances of 0.95 Å. In the final refinement, only the Cd and S atoms were varied anisotropically, the nonhydrogen atoms were varied isotropically, and the hydrogen atoms were placed as a fixed atom contribution with B's

Table III. Positional and Thermal Parameters for Nonhydrogen Atoms for Cd(SMC)$_2$

Atom	x[a]	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cd	0041(1)	0[c]	2514(2)	54.5(7)	144(3)	57.2(9)	−14(3)	19.8(5)	−9(3)
S(1)	3683(4)	2496(14)	1500(6)	51(3)	443(30)	185(8)	−16(9)	−11(4)	−82(15)
S(2)	−3417(4)	−4062(11)	0.4139(5)	54(3)	238(21)	161(7)	−22(7)	18(4)	−23(10)
Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
O(1)	0443(8)	−2402(36)	0698(10)	2.1(2)	C(2)	1721(11)	0958(38)	0539(15)	2.4(3)
O(2)	1245(8)	−2303(37)	−1150(12)	3.0(3)	C(3)	2746(11)	−0072(58)	1148(15)	3.6(3)
O(3)	−0380(8)	2407(37)	4303(11)	2.4(2)	C(4)	3827(17)	3488(56)	−0169(24)	6.4(6)
O(4)	−1262(8)	2187(35)	6110(11)	2.9(3)	C(5)	−1074(14)	1525(41)	4906(20)	2.6(4)
N(1)	1247(9)	2420(43)	1601(13)	2.0(3)	C(6)	−1814(10)	−0469(36)	4136(15)	2.2(3)
N(2)	−1235(9)	−2284(47)	3326(14)	2.6(3)	C(7)	−2462(11)	−1967(35)	5070(15)	2.5(3)
C(1)	1090(13)	−1445(39)	0010(19)	1.9(4)	C(8)	−4426(17)	−1772(55)	3722(22)	6.0(5)

[a] All parameters are ×10^4. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] The y coordinate of Cd fixes the origin.

Table IV. Positional and Thermal Parameters for Nonhydrogen Atoms for Zn(SMC)$_2$

Atom	x[a]	y	z	β_{11}[b]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	0391.6(7)	0[c]	2371.2(9)	42(1)	260(4)	63(1)	−1(2)	19(1)	1(3)
S(1)	3681(2)	−3619(9)	4750(3)	55(2)	705(20)	138(4)	42(5)	32(2)	−8(8)
S(2)	3416(2)	7594(7)	0227(3)	49(2)	386(15)	166(4)	−21(6)	43(2)	20(7)
O(1)	0644(5)	1566(15)	4445(6)	58(4)	251(30)	76(7)	17(11)	16(5)	20(13)
O(2)	1436(6)	0723(16)	6808(6)	111(7)	428(52)	63(7)	53(14)	15(5)	−34(13)
O(3)	1283(4)	2277(15)	1630(5)	47(4)	372(34)	56(6)	4(10)	13(4)	1(14)
O(4)	0036(4)	2688(14)	−0480(6)	33(3)	289(31)	78(7)	7(9)	15(4)	27(14)
N(1)	1149(5)	−3000(18)	3658(7)	42(5)	313(37)	73(8)	−11(11)	22(5)	−55(16)
N(2)	1190(5)	5324(22)	−1800(7)	47(4)	311(39)	64(7)	−34(14)	28(4)	−22(19)
C(1)	1784(7)	−1989(22)	5089(9)	49(6)	308(45)	75(10)	7(14)	27(6)	1(18)
C(2)	1248(7)	0248(34)	5481(8)	55(6)	335(46)	70(9)	−6(21)	24(6)	−6(27)
C(3)	2853(8)	−1129(29)	5020(11)	47(7)	464(55)	117(13)	−1(17)	3(8)	24(24)
C(4)	4056(9)	−4955(47)	6530(13)	80(8)	564(63)	183(17)	42(35)	2(9)	16(52)
C(5)	1731(6)	4329(18)	−0309(8)	35(5)	292(55)	63(9)	−6(12)	25(6)	−14(15)
C(6)	0926(7)	3054(19)	0307(8)	46(6)	186(37)	61(9)	15(13)	23(6)	1(16)
C(7)	2317(7)	6389(23)	0704(9)	34(5)	322(44)	93(11)	−46(14)	22(6)	−54(20)
C(8)	4316(8)	5054(44)	0870(15)	63(7)	492(58)	282(22)	20(33)	70(11)	−8(58)

[a] All parameters are ×10^4. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [c] The y coordinate of Zn fixes the origin.

set at 4.0 Å^2. Inspection of the observed and calculated structure amplitudes near the end of the refinement indicated no significant error in the data due to secondary extinction. In the final cycle of refinement, no parameter shift was greater than 0.1 times its estimated standard deviation. A difference Fourier calculated at the end of the refinement by subtracting out all 33 atoms of the asymmetric unit did not show any peak higher than 0.8 e/Å^3 except for three peaks of about 1.2 e/Å^3 around the cadmium atom and one of about the same density around atom O(3). The final agreement factors are $R_1 = R_2 = 0.052$. The positional and thermal parameters derived from the final cycle of least squares are presented in Table **III**. The fractional coordinates of the hydrogen atoms and a list of observed and calculated structure amplitudes are available.[36]

Zn(SMC)$_2$. The Zn and both S atoms were located from a Patterson function and their positions were refined isotropically ($R_1 = 0.292$, $R_2 = 0.355$). A subsequent difference Fourier map showed the positions of all remaining nonhydrogen atoms. Anisotropic refinement of all nonhydrogen atoms reduced R_1 and R_2 to 0.066 and 0.075, respectively. At this stage, it was apparent that we had chosen the wrong enantiomer since the coordinates corresponded to D-SMC rather than to L-SMC. The original coordinates (x,y,z) were reversed to ($-x,-y,-z$) and refinement as before gave $R_1 = 0.064$ and $R_2 = 0.073$. Most of the hydrogen atoms could be located in a subsequent difference Fourier map, the remaining ones being calculated on the same criteria already mentioned (vide supra). Since the crystal decomposed during data collection (see Table II) in a nonlinear way, no correction for decay was attempted. In the final refinement, the 16 independent hydrogen atoms were included in the least-squares calculation as a "fixed atoms" contribution, resulting in R factors R_1 and R_2 of 0.059 and 0.067, respectively. There was no indication of secondary extinction. In the final cycle of least squares, no atomic parameter underwent a shift of more than 5% of its estimated standard deviation. A final difference Fourier was featureless, with its highest peak of density 0.67 e/Å^3 around the Zn atom. The positional and thermal parameters derived from the final cycle of least-squares are presented in Table IV. The positional parameters of the hydrogen atoms and a list of observed and calculated structure amplitudes are available.[36]

Results and Discussion

Cd(SMC)$_2$. The structure consists of Cd(SMC)$_2$ units linked together by Cd–O(carboxylate) bonds to form a two-dimensional polymer as shown in Figure 1. The geometry around each cadmium atom (see Figure 2) is octahedral with four short equatorial and two longer apical bonds. The pertinent bond lengths and angles are listed in Table V. The base plane is formed by Cd–N(amino) and Cd–O(carboxylate) bonds ranging from 2.26 (1) to 2.28 (2) Å. The coordination around the metal is completed by two oxygen atoms (carboxylate oxygen atoms belonging to neighboring molecules) in apical positions at longer Cd–O distances of 2.45 (1) and 2.47 (2) Å. The octahedral geometry around the metal is not severely distorted, with trans angles ranging from 176.3 (7) to 179.2 (6)°, and cis angles from 75.1 (6) to 95.2 (4)°. The coordination at the metal found in this structure is very similar to that found in Cd(L-met)$_2$[29] where equatorial Cd–O and Cd–N bonds range from 2.269 (5) to 2.301 (5) Å while apical Cd–O distances are 2.445 (5) and 2.524 (5) Å. A least-squares plane calculation involving N(1), N(2), O(1), and O(3) shows that the two nitrogen atoms are 0.028 Å below the best plane, while the two oxygen atoms are 0.028 Å above it. The cadmium atom

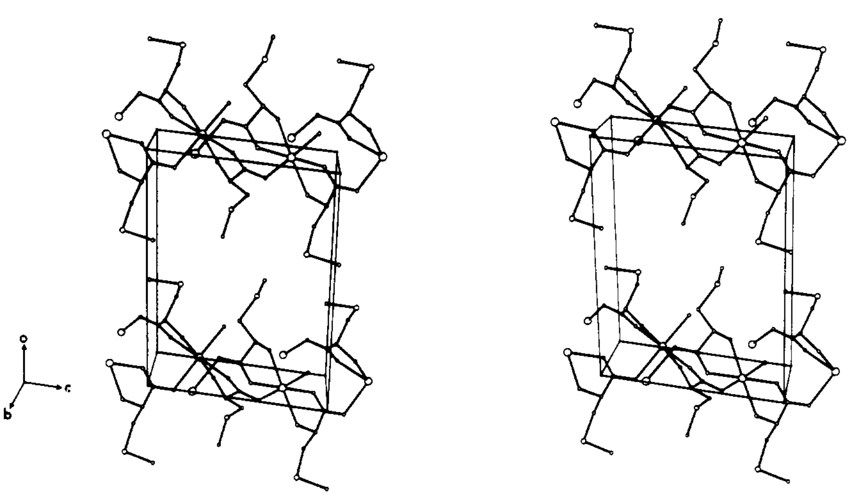

Figure 1. Stereoscopic pair of drawings showing the polymeric nature of the complex Cd(SMC)$_2$, which extends approximately in the crystallographic *b–c* plane.

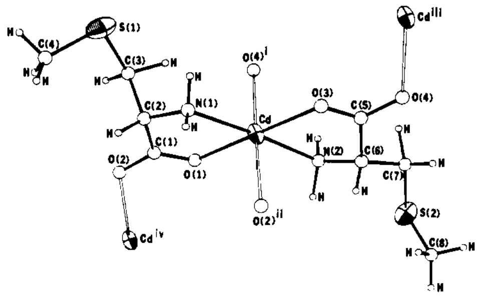

Figure 2. View of the coordination around the cadmium center in Cd(SMC)$_2$. The thermal ellipsoids for Cd and S atoms are scaled at the 40% probability level. Other atoms are represented as circles of arbitrary size. Atom numbering and Roman superscripts are consistent with text and tables.

is displaced 0.044 Å above this plane in the direction of the apical O(4) oxygen atom.

The geometry of the SMC ligands is normal, and the relatively high standard deviations for bonds and angles preclude any detailed discussions. A list of the dihedral angles of interest is presented in Table VI. The terminal *S*-methyl groups, as can be seen in Figure 1, are approximately located in the central region of the cell. There is no intermolecular interaction involving the sulfur atoms. The nearest nonhydrogen atoms to S(1) and S(2) are a methyl carbon atom at 3.82 Å and a carboxylate oxygen atom at 3.79 Å, respectively. As expected, there are very few hydrogen bonds in the structure; only one hydrogen atom on each amino nitrogen atom is hydrogen bonded. The relevant distances and angles are given in Table V. Atom H(1) bonded to N(2) appears to participate in a bifurcated hydrogen bond, being a donor atom for two O(3) atoms in different molecules.

Zn(SMC)$_2$. The structure of Zn(SMC)$_2$, shown in Figure 3, can be described as a one-dimensional polymer running around a twofold screw axis. Its backbone is made of zinc atoms alternating with the carboxylate group of one SMC ligand:

$$\cdots\text{O–Zn–O–C–O–Zn–O}\cdots$$

The other SMC ligand, being terminal, does not participate in the propagation of the chain. The geometry of the zinc atom can be seen in Figure 4. The zinc atom is five-coordinate, a geometry relatively less common for this metal than tetrahedral or octahedral. The geometry at the metal centers can be regarded as trigonal bipyramidal (TBP) rather than square pyramidal (SP). In the ideal TBP, there is one angle of 180°, three of 120°, and six of 90°, while in the ideal SP[37] geometry, there are two angles of 160°, four of 100°, and five of 88.4°. From Table VII, where the main bond lengths and angles involved in this structure are gathered, it can be seen that the geometry at the zinc atom is nearer to TBP than to SP. Each zinc atom is bonded to three SMC moieties through Cd–N(amino) and Cd–O(carboxylate) bonds of lengths ranging from 1.980 (7) to 2.125 (6) Å. These distances are typical of

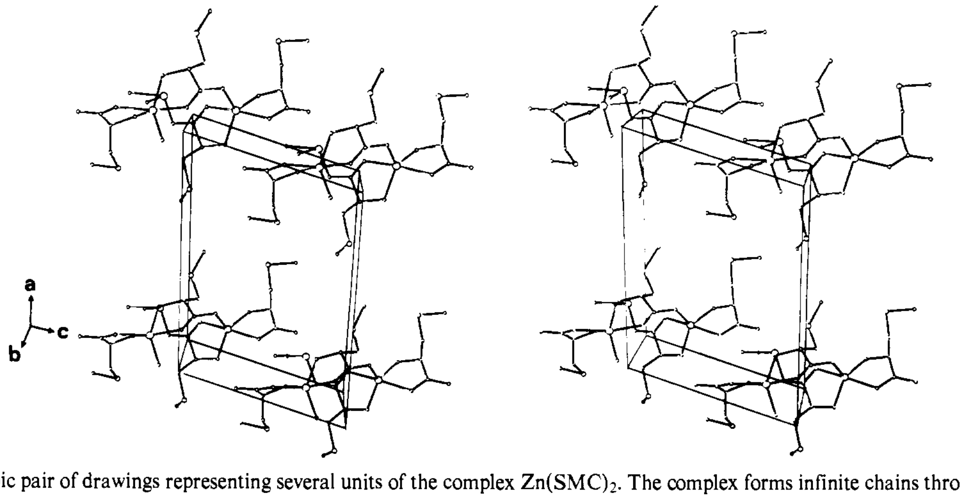

Figure 3. A stereoscopic pair of drawings representing several units of the complex Zn(SMC)$_2$. The complex forms infinite chains through a twofold screw axis coincident to the crystal *b* axis.

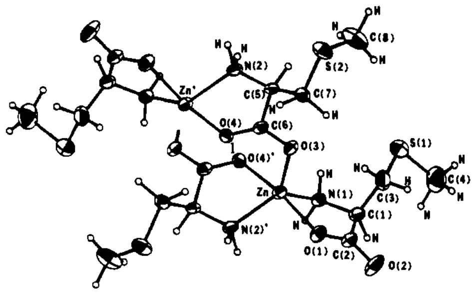

Figure 4. The coordination at the zinc centers in Zn(SMC)$_2$. Thermal ellipsoids are shown at the 40% probability level. Hydrogen atoms are represented as circles of arbitrary size. The broken bond between Zn′ and O(3)′ means that O(3)′ is bonded to a Zn atom located one unit cell below Zn′.

Table V. Interatomic Distances (Å) and Angles (deg) for Cd(SMC)$_2$

Atoms[a]	Distance	Atoms	Distance
Cd-O(1)	2.275(13)	Cd-N(2)	2.273(16)
Cd-O(3)	2.263(13)	Cd-O(4)^{I}	2.455(14)
Cd-N(1)	2.283(16)	Cd-O(2)^{II}	2.470(15)
N(1)-C(2)	1.48(2)	N(2)-C(6)	1.49(2)
C(1)-C(2)	1.54(2)	C(5)-C(6)	1.55(2)
C(2)-C(3)	1.52(2)	C(6)-C(7)	1.53(2)
C(3)-S(1)	1.81(2)	C(7)-S(2)	1.82(2)
S(1)-C(4)	1.75(2)	S(2)-C(8)	1.79(3)
C(1)-O(1)	1.25(2)	C(5)-O(3)	1.24(2)
C(1)-O(2)	1.26(2)	C(5)-O(4)	1.28(2)
Atoms	Angle	Atoms	Angle
O(3)-Cd-N(2)	75.1(6)	O(2)^{II}-Cd-N(2)	88.5(5)
N(2)-Cd-O(1)	104.6(6)	O(2)^{II}-Cd-O(1)	94.5(4)
O(1)-Cd-N(1)	75.1(6)	O(2)^{II}-CdN(1)	87.9(5)
N(1)-Cd-O(3)	105.1(6)	O(2)^{II}-Cd-O(3)	84.7(5)
O(4)^{I}-Cd-N(2)	89.1(5)	O(1)-Cd-O(3)	179.2(6)
O(4)^{I}-Cd-O(1)	85.6(5)	N(1)-Cd-N(2)	176.3(7)
O(4)^{I}-Cd-N(1)	94.5(5)	O(4)^{I}-Cd-O(2)^{II}	177.6(6)
O(4)^{I}-Cd-O(3)	95.2(4)		
Cd-N(1)-C(2)	112(1)	Cd-N(2)-C(6)	109(1)
Cd-O(1)-C(1)	117(1)	Cd-O(3)-C(5)	116(1)
N(1)-C(2)-C(1)	112(1)	N(2)-C(6)-C(5)	109(1)
N(1)-C(2)-C(3)	109(1)	N(2)-C(6)-C(7)	112(2)
C(1)-C(2)-C(3)	107(2)	C(5)-C(6)-C(7)	114(1)
C(2)-C(3)-S(1)	113(2)	C(6)-C(7)-S(2)	113(1)
C(3)-S(1)-C(4)	100(1)	C(7)-S(2)-C(8)	102(1)
C(2)-C(1)-O(1)	120(2)	C(6)-C(5)-O(3)	118(2)
C(2)-C(1)-O(2)	116(2)	C(6)-C(5)-O(4)	116(2)
O(1)-C(1)-O(2)	123(2)	O(3)-C(5)-O(4)	126(2)
C(1)-O(2)-Cd^{IV}	121(1)	C(5)-O(4)-Cd^{III}	118(1)

Hydrogen bonding atoms	Distances		Angles
A-B . . . C	A . . . C	B . . . C	A-B-C
N(1)-H(2)· · ·O(1)^{V}	2.94(3)	2.03	169
N(2)-H(9)· · ·O(3)^{VI}	3.00(3)	2.36	128
N(2)-H(9)· · ·O(3)^{I}	3.04(2)	2.23	150

[a] Roman superscripts refer to atoms in the following positions. I: $-x, y - ½, 1 - z$; II: $-x, ½ + y, -z$; III: $-x, ½ + y, 1 - z$; IV: $-x, y - ½, -z$; V: $x, 1 + y, z$; VI: $x, y - 1, z$.

Table VI. Dihedral Angles (deg) for Cd(SMC)$_2$

Atoms	Angle	Atoms	Angle
N(1)-C(2)-C(3)-S(1)	−71[a]	N(2)-C(6)-C(7)-S(2)	−62
N(1)-C(2)-C(1)-O(1)	−20	N(2)-C(6)-C(5)-O(3)	39
N(1)-C(2)-C(1)-O(2)	158	N(2)-C(6)-C(5)-O(4)	−143
C(2)-C(3)-S(1)-C(4)	−67	C(6)-C(7)-S(2)-C(8)	−85
Cd-N(1)-C(2)-C(3)	−101	Cd-N(2)-C(6)-C(7)	−162
Cd-N(1)-C(2)-C(1)	17	Cd-N(2)-C(6)-C(5)	−36
Cd-O(1)-C(1)-C(2)	11	Cd-O(3)-C(5)-C(6)	−21
Cd-O(1)-C(1)-O(2)	−166	Cd-O(3)-C(5)-O(4)	162

[a] Values are taken as positive when far atom rotates anticlockwise relative to near atom to be ellipsed.

Table VII. Interatomic Distances (Å) and Angles (deg) for Zn(SMC)$_2$

Atoms[a]	Distance	Atoms	Distance
Zn-O(1)	2.090(6)	Zn-N(1)	2.087(9)
Zn-O(4)^{I}	2.125(6)	Zn-N(2)^{I}	2.035(7)
Zn-O(3)	1.980(7)		
N(1)-C(1)	1.48(1)	N(2)-C(5)	1.49(1)
C(1)-C(2)	1.50(2)	C(5)-C(6)	1.54(1)
C(1)-C(3)	1.53(1)	C(5)-C(7)	1.52(1)
C(3)-S(1)	1.80(1)	C(7)-S(2)	1.79(1)
S(1)-C(4)	1.78(1)	S(2)-C(8)	1.79(2)
C(2)-O(1)	1.29(1)	C(6)-O(3)	1.28(1)
C(2)-O(2)	1.25(1)	C(6)-O(4)	1.22(1)
Atoms	Angle	Atoms	Angle
O(3)-Zn-N(2)^{I}	123.1(3)	O(1)-Zn-N(1)	80.2(3)
N(2)^{I}-Zn-N(1)	120.5(4)	O(1)-Zn-N(2)^{I}	94.6(3)
N(1)-Zn-O(3)	116.2(3)	O(4)^{I}-Zn-O(3)	94.8(2)
O(4)^{I}-Zn-O(1)	165.9(3)	O(4)^{I}-Zn-N(1)	91.2(3)
O(1)-Zn-O(3)	99.0(3)	O(4)^{I}-Zn-N(2)^{I}	80.0(3)
Zn-N(1)-C(1)	108.2(7)	Zn^{II}-N(2)-C(5)	113.3(5)
Zn-O(1)-C(2)	113.8(7)	Zn^{II}-O(4)-C(6)	113.5(6)
N(1)-C(1)-C(2)	109.6(8)	N(2)-C(5)-C(6)	109.2(6)
N(1)-C(1)-C(3)	110.8(7)	N(2)-C(5)-C(7)	111.5(8)
C(2)-C(1)-C(3)	107.6(1.0)	C(6)-C(5)-C(7)	111.2(6)
C(1)-C(3)-S(1)	114.6(1.0)	C(5)-C(7)-S(2)	113.8(6)
C(3)-S(1)-C(4)	99.5(7)	C(7)-S(2)-C(8)	99.4(6)
C(1)-C(2)-O(1)	118.6(8)	C(5)-C(6)-O(3)	115.2(7)
C(1)-C(2)-O(2)	117.0(1.0)	C(5)-C(6)-O(4)	120.2(7)
O(1)-C(2)-O(2)	124.4(1.3)	O(3)-C(6)-O(4)	124.4(8)

Hydrogen bonding atoms	Distances		Angles
A-B . . . C	A . . . C	B . . . C	A-B-C
N(2)-H(9) . . . O(2)^{III}	3.23(2)	2.09	159
N(2)-H(10) . . . O(2)^{IV}	2.86(2)	1.91	143

[a] Roman superscripts refer to atoms in the following positions. I: $-x, y - ½, -z$; II: $-x, ½ + y, -z$; III: $x, 1 + z - 1$; IV: $x, y, z - 1$.

five-coordinate zinc complexes: For example, in bis(L-serinato)zinc(II),[38] they range from 1.963 (5) to 2.155 (4) Å, in bis(acetylacetonato)zinc(II),[39] from 1.971 (3) to 2.096 (2), and in glycylglycylglycinatozinc(II)[40] from 1.964 (3) to 2.186 (3) Å. The terminal carboxylate oxygen atom O(2) does not interact with the metal: The shortest intermolecular Zn···O(2) distance is 3.605 (9) Å.

The zinc atom is displaced 0.05 Å in the direction of O(1) from the plane formed by N(1), N(2), and O(3). The bond lengths and angles in the SMC ligands appear normal and are not significantly different from other related ligands.[9,17] None of the sulfur atoms interact with any other atoms in other molecules: the nearest nonhydrogen atoms to S(1) and S(2) are a methylene C at 3.76 (1) Å and a methyl C at 3.76 (1) Å, respectively. Table VIII lists the main dihedral angles for Zn(SMC)$_2$.

As for Cd(SMC)$_2$, the hydrogen bonding scheme found for Zn(SMC)$_2$ is very limited. While neither the amino nitrogen N(1) nor the two sulfur atoms is involved in hydrogen bonding, the amino nitrogen atom N(2) forms a hydrogen bond of length 2.86 (2) Å with a terminal carboxylate oxygen atom O(2), and may also form a weak interaction of length 3.23 (2) Å with the

Table VIII. Dihedral Angles (deg) for $Zn(SMC)_2$

Atoms[a]	Angles	Atoms	Angles
N)-C(1)-C(3)-S(1)	−66[b]	N(2)-C(5)-C(7)-S(2)	−68
N(1)-C(1)-C(2)-O(1)	−28	N(2)-C(5)-C(6)-O(4)	10
N(1)-C(1)-C(2)-O(2)	153	N(2)-C(5)-C(6)-O(3)	−175
C(1)-C(3)-S(1)-C(4)	−75	C(5)-C(7)-S(2)-C(8)	−76
Zn-N(1)-C(1)-C(2)	33	Zn^{I}-N(2)-C(5)-C(7)	−117
2n-N(1)-C(1)-C(3)	−86	Zn^{I}-N(2)-C(5)-C(6)	6
Zn-O(1)-C(2)-C(1)	7	Zn^{I}-O(4)-C(6)-C(5)	−20
Zn-O(1)-C(2)-O(2)	−174	Zn^{I}-O(4)-C(6)-O(3)	165

[a] Roman superscript I refers to atom in the following position: x, $\frac{1}{2} + y$, $-z$. [b] See Table VI for the definition of the dihedral angle.

terminal carboxylate oxygen atom of a different molecule (see Table VII).

The absence of sulfur interaction with the metal in $Cd(SMC)_2$ and $Zn(SMC)_2$ is somewhat surprising in the light of all structural data now available for cysteine (or cysteine derivative) metal complexes; these have clearly shown that the sulfur atom is always involved in metal coordination either in unidentate, bidentate, or tridentate complexes. Relative to cys, the methyl group in SMC and in met should, in principle, increase the electron density at the S atom although it prevents the formation of RS^-. Experimentally, it is found that both in $[Co^{III}(SMC)_2]^+$ [9] and in met complexes containing M-S bonds this bond is always relatively strong,[24,26,27] although it is noteworthy that in the present complexes the amino and carboxyl groups are both deprotonated (i.e., $-NH_2$ and $-COO^-$ rather than $-NH_3^+$ and -COOH), whereas in the methionine complexes containing M-S bonds this is not the case. In all complexes of met^- (i.e., those with $-NH_2$ and $-COO^-$) the ligand coordinates through N and O. The only reported complex of SMC^-, however, does contain Co-S bonds.[9] Despite the fact that SMC has a favorable size for tridentate coordination and is a good potential donor site at the S atom, this study shows that Cd and Zn ions prefer the O and N sites over the S site for metal coordination (in $Cd(SMC)_2$, two weaker Cd-O bonds are still preferred to any Cd-S bond).

Also unexpected by us was the different coordination number for the metal in the two structures. $Cd(SMC)_2$ has basically the same structure as $Cd(\text{L-met})_2$[29], but $Zn(SMC)_2$ and $Zn(\text{L-met})_2$[30] are five- and six-coordinated metal complexes, respectively. In $Zn(SMC)_2$, there is no apparent reason for the metal to be five-coordinate, since this metal much more frequently exhibits distorted tetrahedral or octahedral geometries.

Acknowledgment. This research was supported by U.S. Public Health Service Grant No. ES00895-03 from the National Institute of Environmental Health Sciences.

Supplementary Material Available: A listing of observed and calculated amplitudes for $Cd(SMC)_2$ and $Zn(SMC)_2$ and positional parameters of hydrogen atoms (16 pp). Ordering information is given on any current masthead page.

References and Notes

(1) N. E. Williams and H. G. T. Bridge, *Lancet*, **2**, 602 (1958).
(2) E. Friedheim and C. Corvi, *J. Pharm. Pharmacol.*, **27**, 624 (1975).
(3) H. V. Aposhian, *Science*, **128**, 93 (1958).
(4) J. M. Walshe, *Am. J. Med.*, **21**, 487 (1956).
(5) H. V. Aposhian and M. M. Aposhian, *J. Pharmacol. Exp. Therap.*, **126**, 131 (1959).
(6) R. A. P. Kark, D. C. Poskanzer, and J. Bullock, *New England J. Med.*, **285**, 10 (1971).
(7) H. C. Freeman, G. N. Stevens, and I. F. Taylor, *J. Chem. Soc., Chem. Commun.*, 366 (1974).
(8) H. C. Freeman, F. Huq, and G. N. Stevens, *J. Chem. Soc., Chem. Commun.*, 90 (1976).
(9) P. de Meester and D. J. Hodgson, *J. Chem. Soc., Dalton Trans.*, 618 (1976).
(10) H. M. Helis, P. de Meester, and D. J. Hodgson, *J. Am. Chem. Soc.*, **99**, 3309 (1977).
(11) P. de Meester and D. J. Hodgson, *J. Chem. Soc., Chem. Commun.*, 280 (1976).
(12) P. de Meester and D. J. Hodgson, *J. Am. Chem. Soc.*, **99**, 101 (1977).
(13) P. de Meester and D. J. Hodgson, *J. Chem. Soc., Dalton Trans.*, in press.
(14) P. de Meester, D. J. Hodgson, H. C. Freeman, and C. J. Moore, *Inorg. Chem.*, **16**, 1494 (1977).
(15) J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, **25**, 1857 (1969).
(16) P. J. Birker and H. C. Freeman, *J. Chem. Soc., Chem. Commun.*, 312 (1976).
(17) L. P. Battaglia, A. Bonamartini Corradi, C. G. Palmieri, M. Nardelli, and M. E. V. Tani, *Acta Crystallogr., Sect. B*, **29**, 762 (1973).
(18) C. K. Prout, G. B. Allison, L. T. J. Delbaere, and E. Gore, *Acta Crystallogr., Sect. B*, **28**, 3043 (1972).
(19) M. G. B. Drew and A. Kay, *J. Chem. Soc. A*, 1846 (1971).
(20) M. G. B. Drew and A. Kay, *J. Chem. Soc. A*, 1852 (1971).
(21) Y. S. Wong, P. C. Chieh, and A. J. Carty, *Can. J. Chem.*, **51**, 2597 (1973).
(22) A. J. Carty and N. J. Taylor, *Inorg. Chem.*, **16**, 177 (1977).
(23) N. J. Taylor, Y. S. Wong, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Dalton Trans.*, 438 (1975).
(24) A. J. Carty and N. J. Taylor, *J. Chem. Soc., Chem. Commun.*, 214 (1976).
(25) Y. S. Wong, P. C. Chieh, and A. J. Carty, *J. Chem. Soc., Chem. Commun.*, 741 (1973).
(26) H. C. Freeman and M. L. Golomb, *Chem. Commun.*, 1523 (1970).
(27) R. C. Warren, J. F. McConnell, and N. C. Stephenson, *Acta Crystallogr., Sect. B*, **26**, 1402 (1970).
(28) M. V. Veidis and G. J. Palenik, *Chem. Commun.*, 1277 (1969).
(29) R. J. Flook, H. C. Freeman, C. J. Moore, and M. L. Scudder, *J. Chem. Soc., Chem. Commun.*, 753 (1973).
(30) R. B. Wilson, P. de Meester, and D. J. Hodgson, *Inorg. Chem.*, **16**, 1498 (1977).
(31) W. R. Busing and H. A. Levy, *J. Chem. Phys.*, **26**, 563 (1957).
(32) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(33) For a description of the programs used, see E. D. Estes and D. J. Hodgson, *Inorg. Chem.*, **12**, 2932 (1973).
(34) "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974.
(35) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(36) See paragraph at end of paper regarding supplementary material.
(37) R. J. Gillespie, *J. Chem. Soc.*, 4672 (1963).
(38) D. van der Helm, A. F. Nicholas, and C. G. Fisher, *Acta Crystallogr., Sect. B*, **26**, 1172 (1970).
(39) M. J. Bennett, F. A. Cotton, and R. Eiss, *Acta Crystallogr., Sect. B*, **24**, 904 (1968).
(40) D. van Helm, *Acta Crystallogr., Sect. B*, **26**, 1858 (1970).