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Chemistry of the Cyclopentadienylmetal Carbonyls. III. Organosulfur Derivatives of Cyclopentadienylmolybdenum Tricarbonyl Dimer[1,2]

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We have investigated the reaction of cyclopentadienylmolybdenum tricarbonyl dimer (I) and cyclohexene sulfide with the purpose of obtaining new organosulfur derivatives of this cyclopentadienyl metal carbonyl. From at least ten different products formed in this reaction we were able to isolate and characterize the following compounds: $[C_5H_5Mo(CO)_2SC_6H_{11}]_2$, $C_5H_5Mo(CO)_3SC_6H_{11}$, $[C_5H_5MoS_2C_6H_{10}]_2$, and a second isomer of the formula $[C_5H_5MoS_2C_6H_{10}]_2$. Possible structures for these compounds are discussed. Two other products of this reaction were shown by analyses to have the formulas $C_5H_5Mo(CO)_3S_2C_6H_{10-11?}$ and $[C_5H_5MoS_3C_6H_{10-11?}]_2$; no obvious structures are suggested for these two substances by their formulas. Another compound was obtained through air oxidation of the crude products from this reaction. This material was a highly stable orange crystalline compound whose formula is $[C_5H_5MoSO]_2$; its structure is suggested to be similar to the oxygen analog $[C_5H_5MoO_2]_2$ prepared by Cousins and Green.

Two papers have reported organosulfur derivatives of cyclopentadienylmolybdenum tricarbonyl dimer (I). In the first the reactions of cyclopentadienylmolybdenum tricarbonyl hydride and alkyl disulfides were shown to give the dimeric products $[C_5H_5Mo(CO)_2SR]_2$ ($R = CH_3$, C_2H_5, n-C_4H_9).[3] The second paper reported the reaction of I and methyl disulfide or bistrifluoromethyldithietene to give $[C_5H_5Mo(SCH_3)_2]_2$ and $[C_5H_5MoS_2C_2(CF_3)_2]_2$, respectively.[4] We report here the reaction of cyclohexene sulfide and I by which we have been able to prepare a variety of other organosulfur derivatives of this metal complex.[5,6]

Experimental Section[7]

Cyclopentadienylmolybdenum tricarbonyl was prepared by the literature method;[8,9] cyclohexene sulfide was obtained from Aldrich Chemical Co. Merck acid-washed alumina was used for chromatographic separations without further purification.

High-resolution infrared spectra were recorded on a Perkin-Elmer Model 421 grating spectrometer using either chloroform solutions (NaCl cells) or KBr disks. Some preliminary spectra were obtained using a Beckman IR-10 spectrometer. Infrared data are given in Table I. Proton nmr spectra were taken on a Varian A-60 spectrometer, using deuteriochloroform solutions.

Molecular weight determinations were made using a Mechrolab osmometer. The samples were prepared as approximately 0.01 *m* solutions in benzene, except for compound VIII which dissolved only to approximately 0.001 *m*.

The Reaction between Cyclopentadienylmolybdenum Tricarbonyl Dimer and Cyclohexene Sulfide.—This reaction was carried out several times, varying the reaction times and ratios of the starting materials. It was found that the same products were formed in each case, but weight ratios did vary somewhat. The description of the experiment that follows is typical of the several reactions that were carried out.

A solution of 52.5 g (0.107 mole) of cyclopentadienylmolybdenum tricarbonyl dimer in 600 ml of benzene was prepared in a 1-l. three-necked flask equipped with a nitrogen inlet, reflux condenser, and stirrer. This solution was treated with 40.0 g (0.274 mole) of cyclohexene sulfide *via* a dropping funnel and then heated to reflux under nitrogen. After about 3 hr evolution of carbon monoxide became very vigorous; this rapid evolution continued for about 1.5 hr. At this time, a 200-ml fraction was removed and stored under nitrogen to be worked up separately. The remainder of the reaction mixture was allowed to reflux for another 30 hr to ensure complete reaction.

We had hoped that the preliminary sampling process would allow us to assess the effect of a variation in reaction time on the nature of the products of this reaction. The 200-ml fraction was examined, using chromatography, in the same manner as the remainder of the sample. (A discussion of this workup follows.) The products of this sample were the same as the products obtained from the remainder of the sample except that a small amount (approximately 8%) of starting material was recovered, indicating that the reaction had not quite been completed in the 4.5 hr at reflux.

The remaining reaction mixture was filtered by gravity while hot into a 1-l. round-bottom flask. After standing overnight under nitrogen, refiltration gave a very small quantity of black cubic crystals. This compound was not identified because of the quantity involved; it is shown by analyses not to contain sulfur, however. The filtrate was evaporated to a volume of 200 ml and placed on a 6 × 115 cm alumina column which had been previously packed with benzene. Eluting with benzene caused four major bands to develop. The eluate from the first band (fraction A) upon evaporation gave a violet-blue liquid. The second band (fraction B) to be eluted was salmon in color. Evaporation of the eluate gave a small quantity of solid that was discarded. However, a larger yield of this fraction was obtained in a previous experiment so that characterization of this compound was possible. The third band, which developed slowly with benzene (fraction C), was eluted with a 5% ether–benzene mixture to give a violet solution. On evaporation, this gave violet crystals. A fourth indistinct band (fraction D) was also eluted with 5% ether–benzene but further chromatographic purification revealed it to be a mixture of the third and fifth bands (C and E). Several other bands which had not separated with benzene were developed with ether–benzene eluents. A fifth band (fraction E) on the column was eluted with 20% ether–benzene. Evaporation of the eluate gave dark purple crystals. The sixth band (fraction F) was eluted with 50% ether–benzene. It gave a

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[1] Previous paper in this series: P. M. Treichel, R. L. Shubkin, K. W. Barnett, and D. Reichard, *Inorg. Chem.*, **5**, 1177 (1966).

[2] Presented at the Second International Conference on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965; Abstracts, p 120.

[3] P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

[4] R. B. King, *J. Am. Chem. Soc.*, **85**, 1587 (1963).

[5] During the course of this work we learned that this reaction had also been studied by R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt.[6]

[6] Mention of this work is made in the abstracts from the Second International Symposium on Organometallic Chemistry, Madison, Wis., Aug 30–Sept 3, 1965, p 118.

[7] Microanalyses were performed by A. Bernhardt Laboratory, Mulheim, Germany, and the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[8] R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press Inc., New York, N. Y., 1965.

[9] We thank the Climax Molybdenum Co. for a gift of $Mo(CO)_6$, a precursor to this material.

brownish black eluate which was evaporated to dryness to give a dark solid. Purifications and properties of the individual fractions are given below.

(a) Fraction A was a violet-blue liquid that could be distilled under high vacuum onto a −78° cold finger. The liquid could not be induced to crystallize either by immersing it in a Dry Ice bath or by dissolving it in an organic solvent and cooling to −78°. The compound was found to decompose in air and no analyses were obtained. However, the properties and infrared spectrum suggest that the compound is the monomer $C_5H_5Mo(CO)_3SC_6H_{11}$ (II).

(b) Fraction B (obtained from a previous reaction) was recrystallized from a benzene–octane solution. This compound was identified as $[C_5H_5Mo(CO)_2SC_6H_{11}]_2$ (III) by analyses and its infrared spectrum.

Anal. Calcd for $C_{24}H_{32}S_2O_2Mo_2$: C, 47.0; H, 4.82; S, 9.64. Found: C, 47.30; H, 5.20; S, 9.76.

(c) Fraction C on evaporation gave 0.845 g of crude sample. This was dissolved in about 10 ml of chloroform and the solution was placed on a 2 × 15 cm alumina column. The chromatogram was developed with benzene. A small orange band was eluted first. Solvent was removed from the yellow eluate leaving orange crystals (IV) which were washed with hexane and dried. The major band from this fraction was violet in color and was also eluted with benzene. Evaporation of this eluate gave a dark violet residue. This residue was dissolved in chloroform and recrystallized under nitrogen. The crystals of $[C_5H_5MoS_2C_6H_{10}]_2$ (V) were washed with hexane and dried. At a temperature of 200° the violet compound darkened and at a temperature of 240° it had completely decomposed to a black residue.

The proton nmr spectrum of this compound showed a single sharp resonance at τ 3.52 due to the protons of the cyclopentadienyl ring and another sharp resonance at τ 8.75 due to the $-CH_2-$ protons of the 1,2-disubstituted cyclohexane ring. A broad resonance due to the $-CH-$ protons was centered about τ 4.7.

Anal. Calcd for $C_{22}H_{30}S_4Mo_2$: C, 43.0; H, 4.89; S, 20.85; mol wt, 614.4. Found: C, 43.25; H, 4.94; S, 20.68; mol wt, 648.5.

(d) Fraction E gave 1.34 g of crude sample. The sample was dissolved in 20 ml of chloroform and chromatographed on a 2 × 45 cm alumina column. The chromatogram was developed with benzene. A small band of compound V eluted first. The major band which was maroon in color eluted next. Evaporation of this eluate gave dark red crystals. A blue band and a dark brown band followed the major product. They were only in trace amounts and were not further investigated.

This compound (VI) was identified as having the same molecular formula as V. It was maroon in color and decomposed at 230° to a black residue.

Anal. Calcd for $C_{22}H_{30}S_4Mo_2$: C, 43.0; H, 4.89; S, 20.83; mol wt, 614.4. Found: C, 43.13; H, 4.72; S, 20.68; mol wt, 573.7.

The proton nmr spectrum of a saturated deuteriochloroform solution of this compound with tetramethylsilane as an internal standard gave a single sharp peak at τ 3.53 due to the protons of the cyclopentadienyl group. Broad peaks due to $-CH-$ protons were observed at approximately τ 4.43, 4.53, and 5.05 and several broad resonances due to $-CH_2-$ protons were observed at approximately τ 7.77, 8.30, and 8.70.

(e) Fraction F gave 3.97 g of crude sample. This sample was dissolved in 25 ml of chloroform and filtered. The filtrate was concentrated by evaporation and placed on a 2 × 45 cm alumina column. The chromatogram was developed with benzene. Elution with benzene (note that fraction F had not previously been found to elute with benzene) caused an orange band to be eluted first. This gave a yellow eluate which crystallized to the orange solid IV. This was recrystallized from a chloroform solution by slow evaporation under nitrogen, filtered, washed with hexane, and dried. The infrared spectra of this orange compound and of the orange compound obtained in fraction C were identical; analytical data showed this compound to have the formula $[C_5H_5MoSO]_2$. The compound decomposed at about 300° to a black residue.

Anal. Calcd for $C_{10}H_{10}O_2S_2Mo_2$: C, 28.97; H, 2.41; O, 7.67; mol wt, 418. Found: C, 28.99; H, 2.42; O, 7.61; mol wt, 406.

The proton nmr spectrum of IV showed only a single sharp resonance due to the cyclopentadienyl protons at τ 3.92.

Two further compounds from this reaction were tentatively identified by analyses only. A compound of proposed molecular formula $C_5H_5Mo(CO)_3S_2C_6H_{10-11?}$ (VII) was found to elute with fraction F; purification by chromatography using 10% ether–benzene eluent served to allow separation of this material from the other components of this fraction. Crystallization of this brown-black material was accomplished from a carbon tetrachloride–octane mixture.

Anal. Calcd for $C_{14}H_{16}O_3MoS_2$: C, 42.7; H, 4.07; S, 16.3. Found: C, 42.3; H, 4.78; S, 16.06.

Further elution of fraction F after separation of IV and VII gave two more bands. The first of these two bands eluted with 20% chloroform–benzene to give a dark maroon eluate which was evaporated to dryness. The residue was dissolved in chloroform and filtered; the filtrate was treated with several milliliters of octane and evaporated under nitrogen to give red-black crystals, $[C_5H_5MoS_3C_6H_{10}]_2$ (VIII). The crystals were filtered, washed with two 10-ml portions of hexane, and dried. The compound decomposed to a black residue without melting at a temperature of about 210°. The proton nmr spectrum was very weak due to low solubility, but it did show a doublet due to the protons of the π-cyclopentadienyl groups at τ 3.46 and a broad peak due to $-CH_2-$ protons at about τ 8.50. The spectrum was too weak to discern $-CH-$ protons.

Anal. Calcd for $C_{22}H_{30}S_6Mo_2$: C, 40.9; H, 4.55; S, 27.3; mol wt, 704. Found: C, 41.08; H, 4.62; S, 27.3; mol wt, 610. The inaccuracy of this molecular weight determination is probably due to the very low solubility of this compound.

The second band to be eluted with the 20% chloroform–benzene eluent was a dark rose color. This fraction was not characterized because of insufficient sample.

Discussion

In contrast to the large number of organosulfur compounds derived from pure metal carbonyls which are known, such derivatives of the cyclopentadienylmetal carbonyls have received little attention. We chose to attempt to expand this area by the preparation, characterization, and structural determination of other organosulfur derivatives of the cyclopentadienylmetal carbonyls.[10] In this paper we report new derivatives of cyclopentadienylmolybdenum tricarbonyl dimer (I).

The reagent cyclohexene sulfide was previously used by King[11] in a preparation of a complex whose composition was later shown to be $Fe_3(CO)_9S_2\cdot Fe_2(CO)_6S_2$.[12] Its use in a reaction with rather mild conditions to give a sulfide complex of iron suggested that this reagent might also serve to give sulfide derivatives of I. However, the reagent proved to be more versatile than anticipated and organosulfur derivatives containing SC_6H_{11} and $S_2C_6H_{10}$ groups were formed; no sulfide complexes were among the products characterized.

Chromatography using alumina proved to be the key by which the separation and purification of the products of this reaction was possible. As might be ex-

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(10) In a recent paper the preparation and X-ray structural determination of a new cyclopentadienyliron sulfide, $[C_5H_5FeS]_4$, is reported: C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *Inorg. Chem.*, **5**, 900 (1966).

(11) R. B. King, *ibid.*, **2**, 326 (1963).

(12) L. F. Dahl and C. H. Wei, *ibid.*, **4**, 493 (1965).

Table I

Infrared Bands (cm^{-1}) of Organosulfur Metal Compounds

II $C_5H_5Mo(CO)_3SC_6H_{11}$[b]

2920 vs, 2865 m, 1975 s, 1905 m, 1445 w, 1258 s, 1095 m, 1010 m

III $[C_5H_5Mo(CO)_2SC_6H_{11}]_2$[c]

3000 vw, 2960 s, 2932 m, 2860 w, 1937 vs, 1888 vs, 1452 vw, 1445 vw, 1422 vw, 1200 w, 1000 w, 900 w, 830 m, 812 s, 720 s

IV $[C_5H_5MoSO]_2$[c]

3080 vw, 1442 w, 1415 m, 1354 w, 1349 vw, 1255 vw, 1052 w, 1022 m, 1007 m, 992 m, 920 s, 895 vs, 850 m, 836 s, 805 vs, 798 vs, 668 w

V $[C_5H_5MoS_2C_6H_{10}]_2$[c]

2918 w, 2910 w, 2850 vw, 1448 vw, 1431 w, 1415 s, 1375 vw, 1291 m, 1250 s, 1212 m, 1172 vw, 1130 w, 1115 m, 1025 m, 1019 s, 998 s, 857 s, 810 s, 788 vs, 738 s, 710 m

VI $[C_5H_5MoS_2C_6H_{10}]_2$[c]

3100 w, 3080 w, 3022 w, 2925 m, 2831 w, 1635 w, 1450 m, 1423 s, 1382 w, 1340 w, 1335 m, 1298 w, 1246 m, 1220 w, 1182 vw, 1175 w, 1132 vw, 1120 w, 1105 vw, 1056 w, 1025 m, 1010 s, 1000 s, 985 m, 975 m, 865 m, 859 m, 830 s, 795 vs, 738 s, 715 m

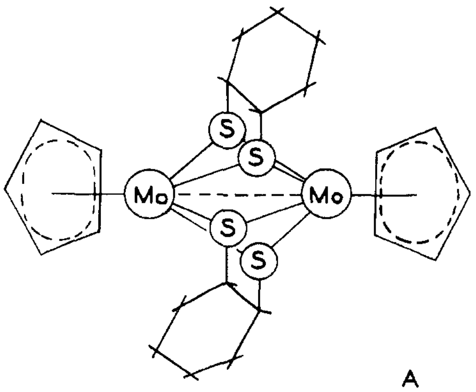
VII $[C_5H_5Mo(CO)_3S_2C_6H_{10-11?}]_x$[a]

3016 s, 2932 m, 2853 w, 2400 vw, 1928 w, 1880 m, 1843 s, 1783 s, 1513 m, 1472 vw, 1441 m, 1421 s, 1220 vs, 1212 vs, 1205 vs, 1040 s, 1007 m, 922 s, 842 s, 750 vs, 660 vs

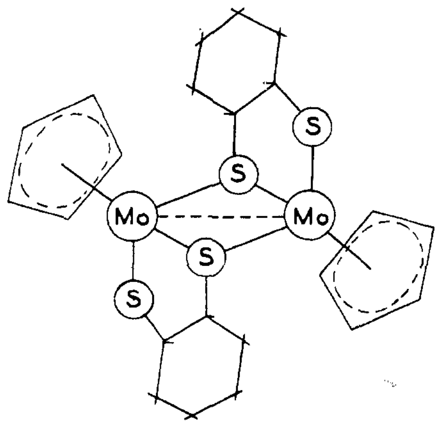
VIII $[C_5H_5MoS_3C_6H_{10}]_2$[a]

3050 w, 3042 w, 1460 w, 1445 m, 1425 s, 1422 s, 1385 vw, 1347 vw, 1257 vw, 1223 vw, 1160 vw, 1120 vw, 1054 s, 1033 s, 1004 s, 955 m, 913 w, 894 w, 866 w, 832 m, 802 vs, 746 m, 720 w

[a] Chloroform solution, NaCl prism. [b] Carbon tetrachloride solution, NaCl prism. [c] KBr pellet.



A



B

Figure 1.—Possible structures of V and VI.

pected this was a rather colorful process as all of the products were highly colored, either purple, red, or black. At least ten different products could be observed on the chromatographic column, but these could not all be isolated and characterized owing to the rather small quantities and low stability of some of these substances.

The two carbonyl-containing compounds $C_5H_5Mo(CO)_3SC_6H_{11}$ (II) and $[C_5H_5Mo(CO)_2SC_6H_{11}]_2$ (III) were the first products to elute from the column. III proved to be similar to the other derivatives of the formula $[C_5H_5Mo(CO)_2SR]_2$ reported earlier.[4] II was an air-unstable purple oil which could be distilled but did not crystallize even at $-78°$. The difficulty in handling this substance was not unexpected, since the compound $C_5H_5Fe(CO)_2SCH_3$ recently prepared by King and Bisnette[13] is air sensitive and also easily converted to the more thermally stable dimer $[C_5H_5Fe(CO)SCH_3]_2$ with loss of carbon monoxide. Compound II was identified by its infrared spectrum, mainly on the basis of the similarity of carbonyl positions and intensities with other $C_5H_5Mo(CO)_3X$ compounds.

Rather unexpectedly two derivatives (V and VI) with the same molecular formula $[C_5H_5MoS_2C_6H_{10}]_2$ were obtained. Both were purple crystalline materials which differed significantly in their infrared and nmr spectra and in their behavior to chromatography, and both were apparently different from a compound of a similar formula reported by Schunn, Fritchie, and Prewitt.[6,14]

Though it is not possible with the available information to assign a structure to each of the two isomers, two probable structures for these isomers can be drawn. These are shown in Figure 1. Structure A containing four bridging sulfur atoms is similar in the coordination of the metal and sulfur to the structure proposed for $[C_5H_5Mo(SCH_3)_2]_2$,[5] $[C_5H_5V(SCH_3)_2]_2$,[15] and $[C_5H_5VS_2C_2(CF_3)_2]_2$.[5] Structure B is similar to that reported for $[C_5H_5CrS_2C_2(CF_3)_2]_2$.[16] It is a diamagnetic structure with each molybdenum atom being two electrons short of an inert gas configuration.

The only possible differentiation between V and VI might be made on the proton nmr spectra of these two materials. The higher symmetry of structure A might lead to a simpler pattern associated with the C_6H_{10} group. Compound V, also the first of these two compounds to eluate from the alumina column,

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(13) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 482 (1965).

(14) R. A. Schunn, private correspondence.

(15) R. H. Holm, R. B. King, and F. G. A. Stone, *Inorg. Chem.*, **2**, 219 (1963).

(16) S. F. Watkins and L. F. Dahl, reported at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1965, Abstracts, p 23-O.

showed a single sharp $-CH_2-$ proton resonance at τ 8.75 whereas the pattern of $-CH_2-$ and $-CH-$ proton resonances for VI was much more complex, consisting of three broad resonances for each type of proton.

Compounds VII and VIII, which have molecular formulas $[C_5H_5Mo(CO)_3S_2C_6H_{10-11}]_x$ and $[C_5H_5MoS_3C_6H_{10-11}]_2$, respectively, on the basis of analytical data could not be assigned structures. VII was not a simple derivative of a $C_5H_5Mo(CO)_3$ group since the infrared spectrum showed bridging carbonyls; unless the latter contains an uncoordinated sulfur atom it is difficult to conceive of a way to use all the possible coordination sites of all sulfur atoms. Lacking further data we regard the molecular structures as only tentatively correct.

The orange crystalline compound $[C_5H_5MoSO]_2$ (IV) appeared not to be formed as a direct product in the reaction since no single band on the original chromatographic column was observed to contain this material. Instead IV appeared in several crude products and was presumably a product of air oxidation of one or several organosulfur molybdenum compounds. This product was exceptionally stable thermally and was also insensitive to oxygen or moisture in the solid state.

A suggestion as to the structure of this compound is seen in the paper of Green and Cousins[17] discussing oxomolybdenum compounds. In this paper a compound of the formula $[C_5H_5MoO_2]_2$ is described; this was obtained with other products on air oxidation of $C_5H_5Mo(CO)_3H$ or $[C_5H_5Mo(CO)_3]_2$. The physical properties and reactivity were not greatly dissimilar from those of IV, and the infrared spectrum appeared rather similar to that of IV, as might be expected if the only difference in these compounds was the presence of two sulfur atoms rather than two oxygen atoms in bridging positions (Figure 2). Specifically the two Mo–O stretching frequencies predicted by Green and Cousins to fall at approximately 920 and 850 or 898 cm^{-1} in the oxo compounds were observed in IV at 920 and 895 cm^{-1}.

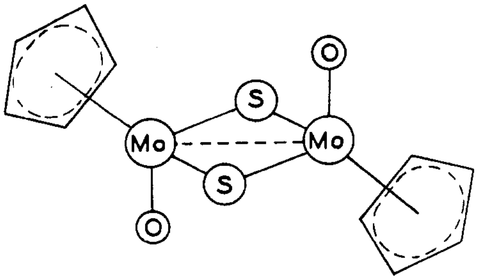

Figure 2.—Structure of $[C_5H_5MoSO]_2$.

The structural formulation of IV in Figure 2 can be seen to fall two electrons short of the inert gas configuration for each molybdenum atom. The sharp C_5H_5 proton resonance indicates this compound is diamagnetic, however.

Acknowledgement.—We are pleased to acknowledge partial support for this work from the National Science Foundation, Washington 25, D. C., through Grant 6051-A.

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[17] M. L. H. Green and M. Cousins, *J. Chem. Soc.*, 1567 (1964).

CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS,
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The Crystal and Molecular Structure of Dichloro(1,10-phenanthroline)zinc

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Crystals of dichloro(1,10-phenanthroline)zinc are monoclinic with four molecules in a unit cell of dimensions $a = 9.73$, $b = 15.67$, $c = 7.97$ A, $\beta = 101° 5'$, space group $P2_1/n$. Three-dimensional data were used, and the structure was solved as a heavy-atom problem. The coordination about the zinc atom is distorted tetrahedral. The 1,10-phenanthroline molecule itself is essentially planar, and the zinc atom departs 0.13 A from this plane. The chlorine atoms are nearly equidistant from the zinc atom. The plane of the zinc and two chlorine atoms makes an angle of 79° with the plane of the 1,10-phenanthroline molecule.

Introduction

The electron paramagnetic resonance technique has provided considerable information about the bonding in paramagnetic transition element complexes.[1] Especially useful data have been obtained when the paramagnetic ion under investigation resides as a substitutional impurity in a diamagnetic lattice. This special utility is a consequence of the fact that magnetic dilution frequently permits the observation of ligand hyperfine structure which can, in turn, be related to bonding parameters. The paramagnetic copper(II) ion has been investigated in a variety of environments and in several instances crystals of the zinc compound have served as the diamagnetic host for these ions. Crystals of copper(II)-doped dichloro(1,10-phenanthroline)zinc (hereafter called $ZnCl_2 \cdot$phen) were obtained and preliminary paramagnetic resonance spectra revealed the presence of abundant hyperfine structure. In order to carry through an analysis of this hyperfine

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[1] W. Low, *Solid State Phys. Suppl.*, **2**, 1 (1960).