vibrations are considerably larger than those observed during the successive deprotonation of either $[Rh(en)_3]I_3$[7] or $[Pt(bipy)(en)]I_2$.[16]

The NH_2 vibrational modes are also affected by deprotonation. The NH_2 stretching and bending vibrations either disappear in the spectra of the singly deprotonated species or are reduced in intensity. As for the doubly deprotonated complexes, $KNi(NHCH_2CO_2)_2$ and $K_2Ni(NHCH_2CH_2CO_2)_2$, since neither of these contain the amino group, no bands characteristic of NH_2 vibrations should be observed. Most probably, the intense bands between 3150 and 3350 cm^{-1} are due to crystal-field splitting of the N–H stretching mode. In the case of $K_2Ni(NHCH_2CO_2)_2$ this vibration appears as a doublet, and in the case of $K_2Ni(NHCH_2CH_2CO_2)_2$, as a triplet.

The Ni–O stretching mode in $Ni(NH_2CH_2CO_2)_2$ has been assigned empirically by Nakamoto[25] to a band at 280 cm^{-1}, but there is some doubt as to whether the corresponding band at 285 cm^{-1} in bis(β-alaninato)nickel(II) could also be assigned to this vibrational mode, especially since analogous bands are not observed in the spectrum of either $KNi(NHCH_2CH_2CO_2)(NH_2CH_2CH_3CO_2)$ or $K_2Ni(NHCH_2CH_2CO_2)_2$. Possibly deprotonation of these complexes causes a reduction in the covalent character of the Ni–O bonds, and the ν(Ni–O) vibrations are shifted to much lower frequencies in the deprotonated complexes. A similar conclusion can be drawn from the frequency shifts of the carboxylate stretching modes.

The asymmetric and symmetric COO stretching vibrations are normally very susceptible to the effects of coordination and intermolecular interaction,[28] and Nakamoto, *et al.*,[14] have suggested that whenever there is a decrease in the covalent character of the Ni–O bonds, there is a corresponding decrease in the frequency separation of the two COO stretching modes. In the spectra of $KNi(NHCH_2CH_2CO_2)(NH_2CH_2CH_2CO_2)$ and $K_2Ni(NHCH_2CH_2CO_2)_2$, the COO asymmetric stretch appears at a lower frequency, and the COO symmetric stretch at a higher frequency, than in the parent $Ni(NH_2CH_2CH_2CO_2)_2$. This is consistent with a weakening of the Ni–O bond with successive deprotonation. A similar weakening of the Ni–O bond is not unequivocably confirmed in the case of the nickel–glycine derivatives, however, where only the asymmetric COO stretching frequency shifts in the expected direction.

Acknowledgments.—This work was supported by the Robert A. Welch Foundation and the U. S. Atomic Energy Commission.

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[28] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 203.

CONTRIBUTION FROM THE OLIN RESEARCH CENTER,
CHEMICALS DIVISION, NEW HAVEN, CONNECTICUT

1,2-Bis-Substituted *o*-Carborane Complexes. II.[1] Nickel(II) and Cobalt(II) Complexes Derived from the Ligand 1,2-Bis(mercapto)-*o*-carborane

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Some nickel(II) and cobalt(II) salts have been found to react readily with 1,2-bis(mercapto)-*o*-carborane in the presence of stabilizing phosphorous ligands or the tetraethylammonium cation to yield square-planar MS_2P_2 and MS_4^{2-} complexes. Electronic spectra of the nickel complexes are discussed.

Introduction

In a previous communication we reported the synthesis of four-coordinate nickel(II) complexes of 1,2-bis(diphenylphosphino)-*o*-carborane and B-bromo-*o*-carboranes.[1] Ligand-exchange data suggested that the order of stability of the series described was $[((C_6H_5)_2P)_2B_{10}H_{10}C_2]NiCl_2 < [((C_6H_5)_2P)_2B_{10}H_{10}C_2]_2NiCl_2 < [((C_6H_5)_2P)_2B_{10}H_9BrC_2]_2NiCl_2 < [((C_6H_5)_2P)B_{10}H_8Br_2C_2]_2NiCl_2 < [((C_6H_5)_2P)_2B_{10}H_7Br_3C_2]_2NiCl_2$. This order is probably a consequence of increased π bonding between phosphorus and nickel due to an increase in the electronegativity of the borane system with increased halogen substitution. It is also conceivable that the observed stability is a result of electron delocalization of a pseudo-aromatic nature involving the –M–P–carborane–P– cyclic system.

Gray and co-workers have reported the electronic structures of stable square-planar complexes of various transition metals with bidentate sulfur ligands capable of extensive π delocalization.[2] The recent synthesis of 1,2-bis(mercapto)-*o*-carborane provides a potential bidentate sulfur ligand comparable to both the phosphino carboranes and the sulfur ligands of Gray, *et al.* It was of interest to attempt to prepare complexes utilizing 1,2-bis(mercapto)-*o*-carborane as the chelating ligand and examine the chemical properties and electronic spectra in order to obtain information on the

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[1] For the first paper in this series see H. D. Smith, Jr., *J. Am. Chem. Soc.*, **87**, 1817 (1965)

[2] H. B. Gray, *Progr. Transition Metal Chem.*, **1**, 240 (1965).

ability of the carborane nucleus to participate in π bonding.

In this paper we report the synthesis and properties of nickel(II) and cobalt(II) complexes of 1,2-bis(mercapto)-*o*-carborane stabilized by phosphorous ligands or the tetraethylammonium cation. The electronic spectra of the nickel complexes are discussed.

Experimental Section

Preparation of Compounds.—1,2-Bis(mercapto)-*o*-carborane was prepared by the method of Smith, Obenland, and Papetti,[3] 1,2-bis(diphenylphosphino)-*o*-carborane according to the procedure of Alexander and Schroeder,[4] and 1,2-bis(diphenylphosphino)ethane according to the method of Chatt and Hart.[5] All other materials were readily obtained from various commercial sources.

All melting points are uncorrected.

$[(C_6H_5)_3P]_2Ni(B_{10}H_{10}C_2S_2)$ (I).—To a solution of 5.2 g (0.02 mole) of triphenylphosphine in 50 ml of ethyl acetate was added 2.49 g of nickel acetate in 10 ml of ethyl alcohol. The resulting green solution was refluxed for 1 min after which 1,2-bis(mercapto)-*o*-carborane (2.08 g) in 10 ml of ethyl acetate was added at once. A green crystalline solid precipitated after 3 min. After washing with successive portions of ethanol, ethyl acetate, and petroleum ether (bp 30–60°) the crystals were dried under vacuum at 100°; yield, 7.1 g (90%); mp 250° dec. *Anal.* Calcd for I: C, 57.79; H, 5.07; B, 13.69; S, 8.10; P, 7.85. Found: C, 57.62; H, 5.20; B, 13.80; S, 7.94; P, 8.06.

$[(C_6H_5)_3P]_2Ni(B_{10}H_9BrC_2S_2)$ (II).—To a solution prepared by mixing 1.65 g of $NiCl_2 \cdot 6H_2O$ in 5 ml of ethanol with 3.64 g of triphenylphosphine in 20 ml of ethyl acetate was added 2.0 g of 1,2-bis(mercapto)monobromo-*o*-carborane[3] in 10 ml of ethyl acetate. After 30 min of refluxing a tan microcrystalline precipitate separated from the dark solution. After washing with ethanol, ethyl acetate, and petroleum ether (bp 30–60°) the crystals were dried over P_2O_5 in a vacuum desiccator; yield, 85%; mp 234° dec. *Anal.* Calcd for II: C, 52.54; H, 4.53; B, 12.46; Br, 9.20. Found: C, 52.71; H, 4.20; B, 12.53; Br, 10.50.

$[(C_6H_5)_2P(B_{10}H_{10}C_2)P(C_6H_5)_2]Ni(B_{10}H_{10}C_2S_2)$ (III).—A solution of 2.08 g of 1,2-bis(mercapto)-*o*-carborane in 10 ml of ethyl acetate was added at once to a refluxing solution of 2.37 g of $NiCl_2 \cdot 6H_2O$ in 10 ml of ethanol. To the resulting purple solution was added 5.14 g of 1,2-bis(diphenylphosphino)-*o*-carborane in 50 ml of ethyl acetate. After 30 min of refluxing the brown precipitate formed was collected by filtration, washed with hot ethanol and ethyl acetate, and dried under vacuum at 100°; yield, 5.0 g (64.5%); mp 380° dec. *Anal.* Calcd for III: C, 43.21; H, 5.18; B, 27.84. Found: C, 43.32; H, 5.27; B, 26.28.

$[(C_6H_5)_2P(B_{10}H_{10}C_2)P(C_6H_5)_2]NiCl_2$ (IV).—A 1:1 mole ratio mixture of 1,2-bis(diphenylphosphino)-*o*-carborane and nickel chloride hexahydrate was mixed in ethyl acetate solution and refluxed for several hours. The red crystalline precipitate obtained was washed with hot ethanol followed by hot benzene and low-boiling petroleum ether. The product was air dried; yield, 50%; mp 340° dec. *Anal.* Calcd for IV: C, 48.60; H, 4.70; B, 16.80; Cl, 11.04. Found: C, 48.61; H, 4.88; B, 17.45, Cl, 11.00.

$[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]Ni(B_{10}H_{10}C_2S_2)$ (V).—A 3.9-g sample of 1,2-bis(diphenylphosphino)ethane in 20 ml of ethyl acetate was added at once to a hot solution containing 2.08 g of 1,2-bis(mercapto)-*o*-carborane in 25 ml of ethyl acetate and 2.37 g of $NiCl_2 \cdot 6H_2O$ in 10 ml of ethanol. A yellow precipitate formed after a few minutes. The product was recrystallized from nitromethane and vacuum dried over P_2O_5; yield, 4.5 g (68%); mp 375° dec. *Anal.* Calcd for V: C, 50.65; H, 5.16; P, 9.33. Found: C, 51.04; H, 5.17; P, 9.17.

$[(C_2H_5)_4N]_2Ni(B_{10}H_{10}C_2S_2)_2$ (VI).—To an ethyl acetate solution of 0.02 mole of 1,2-bis(mercapto)-*o*-carborane was added an ethanol solution of 0.01 mole of $NiCl_2 \cdot 6H_2O$. The resulting deep red solution was refluxed for 30–60 min after which a solution of 0.03 mole of tetraethylammonium bromide in ethanol was added and reflux was continued for 10–15 min. The tan precipitate was collected by filtration and recrystallized from nitroethane; yield, 3.0 g (41%); mp 320° dec. *Anal.* Calcd for VI: C, 32.85; H, 8.21; B, 29.79. Found: C, 32.90; H, 8.20; B, 29.23.

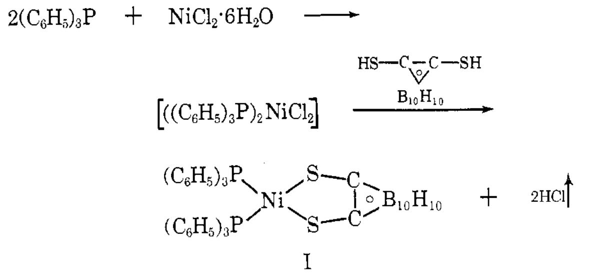
$[(C_6H_5)_2P(B_{10}H_{10}C_2)P(C_6H_5)_2]Co(B_{10}H_{10}C_2S_2)$ (VII).—This compound was prepared in a manner similar to that of III from $Co(ClO_4)_2 \cdot 6H_2O$; yield, 64.0%; mp 353° dec. *Anal.* Calcd for VII: C, 43.80; H, 5.21; B, 28.20. Found: C, 43.45; H, 5.32; B, 27.60.

$[(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2]Co(B_{10}H_{10}C_2S_2)$ (VIII).—To a hot solution of 1,2-bis(mercapto)-*o*-carborane in heptane (2.08 g in 25 ml) was added a concentrated ethanol solution of $Co(ClO_4)_2 \cdot 6H_2O$ (3.65 g). To this mixture was added a solution of 4.0 g of 1,2-bis(diphenylphosphino)ethane in 20 ml of ethyl acetate. After 5 min of refluxing an orange-yellow precipitate formed. This was collected, washed with ethanol and ethyl acetate, and recrystallized from a mixture of acetonitrile and methanol; yield, 40%; mp 350° dec. *Anal.* Calcd for VIII: C, 50.65; H, 5.13; B, 16.30. Found: C, 50.95; H, 5.23; B, 16.05.

$[(C_2H_5)_4N]_2Co(B_{10}H_{10}C_2S_2)_2$ (IX).—Addition of a concentrated solution of $Co(ClO_4) \cdot 6H_2O$ in ethanol to an equimolar quantity of 1,2-bis(mercapto)-*o*-carborane in heptane followed by addition of excess tetraethylammonium bromide in ethanol resulted in the precipitation of green crystals. These were recrystallized from nitromethane; yield, 50%; mp 350° dec. *Anal.* Calcd for IX: C, 32.80; H, 8.20; N, 3.83. Found: C, 32.95; H, 8.24; N, 3.63.

Results and Discussion

General Information.—When triphenylphosphine was mixed with nickel chloride in ethyl acetate–methanol solution and allowed to stand for several hours, greenish blue crystals of bis(triphenylphosphino)nickel chloride were obtained. If, however, the ligand 1,2-bis(mercapto)-*o*-carborane[3] was added a few minutes after mixing the triphenylphosphine and nickel chloride, an olive-colored crystalline precipitate formed within 10 min. The reaction is represented by



(1)

With the ligand 1,2-bis(mercapto)monobromo-*o*-carborane,[3] bis(triphenylphosphino)nickel(II) chloride yielded the desired analogous complex (II), but precipitation occurred after a much longer time (30 min).

An analogous reaction sequence, in which the chelating ligand 1,2-bis(diphenylphosphino)-*o*-carborane (DPPC) was employed in place of triphenylphosphine, resulted in the formation of the expected P_2S_2 nickel complex (III) with 1,2-bis(mercapto)-*o*-carborane, but only the P_2Cl_2 complex (IV) with 1,2-bis(mercapto)monobromo-*o*-carborane (DMMBC).

The diphosphine, 1,2-bis(diphenylphosphino)ethane

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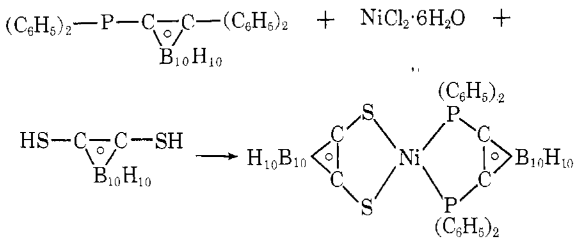
[3] H. D. Smith, Jr., C. O. Obenland, and S. Papetti, *Inorg. Chem.*, **5**, 1013 (1966).

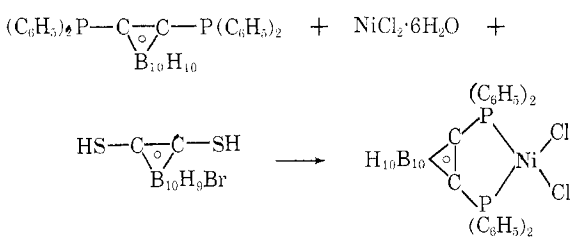
[4] R. Alexander and H. Schroeder, *ibid.*, **2**, 1107 (1963).

[5] J. Chatt and F. A. Hart, *J. Chem. Soc.*, 1378 (1960).



(2)

III



(3)

IV

(TPP), reacted in a fashion similar to DPPC yielding the corresponding P_2S_2 complex (V). All of the compounds synthesized in this work are listed in Table I.

TABLE I

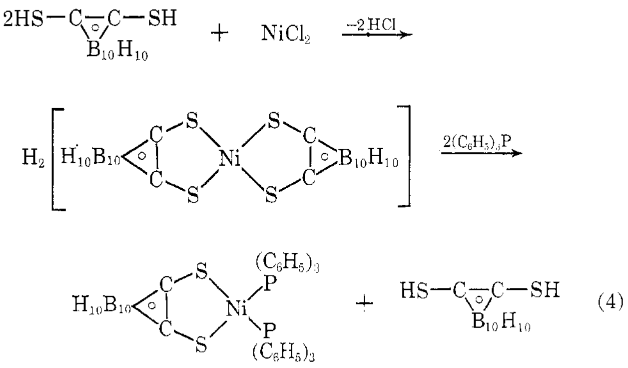
COLORS, DECOMPOSITION POINTS, AND MAGNETIC MOMENTS OF COBALT(II) AND NICKEL(II) COMPLEXES WITH THE LIGANDS DPPC[a] AND DMC[b]

No.	Compd	Color	Mp (dec), °C	μ_{eff}
I	$((C_6H_5)_3P)_2Ni(DMC)$	Olive-green	244	Diamag
II	$((C_6H_5)_3P)_2Ni$-(DMMBC)[c]	Pink-brown	234	Diamag
III	(DPPC)Ni(DMC)	Light brown	380	Diamag
IV	$(DPPC)NiCl_2$	Red	304	Diamag
V	(TPP)Ni(DMC)[d]	Orange-yellow	375	Diamag
VI	$[(C_2H_5)_4N]_2Ni(DMC)_2$	Tan	320	Diamag
VII	(DPPC)Co(DMC)	Orange	353	2.08
VIII	(TPP)Co(DMC)	Orange-yellow	350	2.28
IX	$[(C_2H_5)_4N]_2Co(DMC)_2$	Green	340	5.20

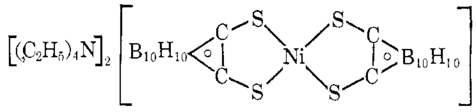
[a] DPPC = 1,2-bis(diphenylphosphino)-*o*-carborane. [b] DMC = $(\mathrm{S{-}C}\underset{\mathrm{B_{10}H_{10}}}{\overset{\diagdown O \diagup}{-\!\!-}}\mathrm{C{-}S})^{2-}$. [c] DMMBC = $(\mathrm{S{-}C}\underset{\mathrm{B_{10}H_{9}Br}}{\overset{\diagdown O \diagup}{-\!\!-}}\mathrm{C{-}S})^{2-}$.
[d] TPP = 1,2-bis(diphenylphosphino)ethane.

Similar NiP_2S_2 complexes have been previously reported.[6-8]

If, instead of initially forming the nickel chloride–phosphine complex in solution, 1,2-bis(mercapto)-*o*-carborane is treated with nickel chloride (acetate or perchlorate), a deep red solution of indefinite stability is obtained. Addition of any of the phosphorous ligands mentioned previously causes precipitation of the respective P_2S_2 nickel complexes. The reaction is believed to proceed as shown in eq 4.



(4)



VI

Addition of tetraethylammonium bromide to the red solution resulted in the precipitation of a compound with an elemental composition corresponding to the salt VI.

TABLE II

CONDUCTIVITY DATA (Λ[a])

Compound	CH_3NO_2	CH_3-CH_2-NO_2	CH_3CN	DMF	CH_2Cl_2
$((C_6H_5)_3P)_2Ni(DMC)$	10.0		110.5	60.0	<0.17
$((C_6H_5)_3P)_2Ni$-(DMMBC)	21.0	28.9	107.5	59.8	<0.17
(DPPC)Ni(DMC)		31.9	Insol	58.8	Insol
(TPP)Ni(DMC)	5.66		Insol	4.90	<0.1675
$[(C_2H_5)_4N]_2Ni(DMC)_2$	156.0		Insol	124.0	Insol
$[(C_2H_5)_4N]_2Co(DMC)_2$		152.0		137.0	Insol
$((C_6H_5)_3P)_2NiCl_2$				69.4	
$((C_6H_5)_2PS_2)_2Ni$				100.0	

[a] Units: $cm^2\ mole^{-1}\ ohm^{-1}$, in $\sim 10^{-3}$ *M* solutions.

Conductivity data (Table II) indicate that VI behaves as a bi-univalent salt in nitromethane or dimethylformamide. The diamagnetism of VI suggests that the anion is square-planar, a supposition in agreement with the electronic spectral data as discussed in the following section.

Only (TPP)Ni(DMC) in the P_2S_2 systems showed nonelectrolyte behavior in solvents of different ionizing abilities. $((C_6H_5)_3P)_2Ni(DMC)$ was a nonconductor in nitromethane or dichloromethane but showed appreciable conductivity in acetonitrile and dimethylformamide as did (DPPC)Ni(DMC) and $((C_6H_5)_3P)_2Ni$-(DMMBC). There is obviously a relationship between the observed conductivities and the stabilizing abilities of the phosphorous ligands. However, additional information is necessary before any conclusions can be made.

In order to evaluate the effect of electronegative groups bonded to the carborane cage on the coordinating tendency of the attached sulfur atoms, an attempt was made to synthesize a series of complexes of which compounds I and II represent the first and second members, respectively. However, no stable mixed complexes were isolated when di- and tribromobis(mercapto)-*o*-carboranes were treated with nickel chloride in the presence of the phosphorous ligands mentioned previously. If it is assumed that the initial reaction between the metal ion and the sulfur ligand is the formation of a coordinate covalent bond, then the decrease in reactivity of the mercaptocarboranes with increased bromine

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(6) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **2**, 1227 (1963); **3**, 814 (1964).

(7) A. Davison and D. V. Howe, *Chem. Commun.*, 290 (1965).

(8) V. P. Mayweg and G. N. Schrauzer, *ibid.*, 640 (1966).

substitution can be attributed to the reduced nucleophilicity of the sulfur atom due to an increase in the electronegativity of the borane nucleus.

The cobalt analogs of compounds III, V, and VI (VII, VIII, and IX), were readily prepared from cobaltous perchlorate in the same manner as the nickel complexes. The triphenylphosphine analog (II) could not be obtained; instead a light blue compound with an infrared spectrum and elemental composition corresponding to $((C_6H_5)_3P)_2Co(ClO_4)_2$ formed when the mixture was allowed to stand for a short period.

Compound IX was a bright green crystalline solid with a magnetic moment corresponding to three unpaired electrons while VII and VIII were orange crystalline solids with magnetic moments indicative of one unpaired electron. The geometry of the carborane moiety is almost certain to force a square-planar configuration in the complexes containing two bidentate carborane-based ligands. The high value for the magnetic moment found for $Co(DMC)_2^{2-}$ coupled with the observation that all of the analogous carborane complexes appear to be square-planar suggest that $Co(DMC)_2^{2-}$ may be an example of a high-spin square-planar cobaltous complex. A detailed spectral analysis of the cobalt complexes will be presented at a later time.

Spectra.—The principal factors involved in the stabilization of the square-planar geometry in transition metal complexes, although not as yet completely resolved, are believed to be (1) involvement of the metal out-of-plane orbitals (d_{xz}, d_{yz}, p_z) in an intensive π-orbital network encompassing the entire complex[2] and (2) the nature of the metal–ligand bond (predominancy of σ or π character).[9,10] The former factor is believed to be most important in complexes involving the α-dithiodiketones[10] and related ligands.[2] Gray and co-workers have undertaken a detailed investigation of square-planar complexes of this type. Of particular pertinency are the compounds of d^8 metals with maleonitriledithiolate (MNT^{2-}) and toluene-3,4-dithiolate (TDT^{2-}).[2]

Complexes with isomaleonitriledithiolate (i-MNT^{2-})[11] and 2,3-dimercaptopropanol (DMP^{2-})[12] provide examples of the latter type, in which stability is apparently a function of the nature of the metal–ligand bond.

Theoretically the carborane nucleus, because of its delocalized nature and electron deficiency, should be an effective ligand in distributing charge if a means of π interaction with the electron source exists. However, an examination of *m*- and *p*-[α-carboranyl]benzoic acids and related systems by Hawthorne and coworkers[13] provided no evidence for electron delocalization by interaction of the aryl group with the highly delocalized *o*-carborane nucleus, although it has been postulated that back-bonding by π substituents on the isoelectronic $B_{12}H_{12}^{2-}$ is possible.[14] In the *o*-dithiocarborane, a potential means of π interaction exists by virtue of the presence of the two sulfur atoms with their inherent ability to accept electrons back donated from the metal. It was believed that the efficacy of π delocalization of the dithiocarborane moiety would be reflected in the nature of the metal–sulfur interaction. Consequently, the electronic spectrum of $Ni(DMC)_2^{2+}$ was investigated in order to ascertain the type of metal–sulfur interaction. An empirical comparison of this spectrum with those of four-coordinate, square-planar dithio-containing compounds in which, on one hand, the nickel–sulfur bonds are of the σ type [bis(1-propanol-2,3-dithionato)nickel(II)][12] and, on the other hand, complexes in which the nickel–sulfur bonds have a large amount of π character [bis(maleonitriledithiolate)nickel(II)][2] indicated that the carborane complex resembled much more the former type—the metal–sulfur bond had predominantly σ character. Further, from this lack of π character of the metal–sulfur bond it is inferred that the carborane nucleus does not provide an effective network for π delocalization. Consequently, the transitions are assigned on the basis of a system in which there is no π interaction between the metal and the ligand. The adopted order of energy levels follows the scheme proposed by Gray and Ballhausen.[15] It should be mentioned, at this point, that it is *not* the intention of the authors to become involved in the controversy regarding the ordering of the energy levels in square-planar complexes. Any changes in the d-orbital order will not seriously affect the assignments or the conclusions presented in this paper. The energy level scheme orders the d orbitals by increasing energy as $d_{xz}, d_{yz} < d_{z^2} < d_{xy} < d_{x^2-y^2}$. Three d–d absorptions are expected corresponding to the one-electron transitions from the various d orbitals to the $d_{x^2-y^2}$ level. All of these are discernible as well as two charge-transfer bands. The assignments are given in Table III.

The stability of square-planar stereochemistry in the DMC–Ni system was revealed upon studying the electronic spectrum in nitromethane and N,N-dimethylformamide (DMF). As shown in Table III, the spectrum was essentially the same. Addition of pyridine to the DMF solution containing the ion $Ni(DMC)_2^{2-}$ caused no change in the spectrum and tetraethylammonium salt was recovered on concentration of the solution. No alterations were observed even when a concentrated methanol solution of CN^- was added to $Ni(DMC)_2^{2-}$ in DMF. Finally, attempted oxidation with bromine in dimethyl sulfoxide resulted in the decomposition of the complex.

Several neutral square-planar complexes involving one *o*-carborane-1,2-dithiolato moiety in conjunction with uncharged phosphorous ligands have been synthesized and their electronic spectra evaluated (Table IV). It is interesting to note that, in every case, these

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[9] A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, **3**, 814 (1964).

[10] G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, **87**, 3585 (1965).

[11] B. G. Werden, E. Billig, and H. B. Gray, *Inorg. Chem.*, **5**, 79 (1966).

[12] D. L. Leussing, *J. Am. Chem. Soc.*, **81**, 4208 (1959).

[13] M. F. Hawthorne, T. E. Berry, and P. A. Wegner, *ibid.*, **87**, 4746 (1965).

[14] H. E. Longuet-Higgins and M. D. Roberts, *Proc. Roy. Soc.* (London), **A230**, 110 (1965).

[15] H. B. Gray and C. J. Ballhausen, *J. Am. Chem. Soc.*, **85**, 260 (1963).

TABLE III

ELECTRONIC SPECTRA FOR TETRAETHYLAMMONIUM BIS(o-CARBORANE-1,2-DITHIOLATO)NICKEL(II)

Solvent	Absorption, cm^{-1}	ε	Assignment
Nujol	13,900	...	$^1A_{1g} \rightarrow {}^1A_{2g}$
	20,400	...	$^1A_{1g} \rightarrow {}^1B_{1g}$
	23,300	...	$^1A_{1g} \rightarrow {}^1E_g$[a]
	29,400	...	$^1A_{1g} \rightarrow {}^1A_{2u}$
	34,500	...	$^1A_{1g} \rightarrow {}^1E_u$
CH_3NO_2	13,700	30	$^1A_{1g} \rightarrow {}^1A_{2g}$
	20,400	70	$^1A_{1g} \rightarrow {}^1B_{1g}$
	22,500	260	$^1A_{1g} \rightarrow {}^1E_g$[a]
DMF	13,500	49	$^1A_{1g} \rightarrow {}^1A_{2g}$
	20,200	110	$^1A_{1g} \rightarrow {}^1B_{1g}$
	23,300	240	$^1A_{1g} \rightarrow {}^1E_g$[a]
	30,800	22,000	$^1A_{1g} \rightarrow {}^1A_{2u}$
DMF + pyridine	13,500	54	$^1A_{1g} \rightarrow {}^1A_{2g}$
	20,000	132	$^1A_{1g} \rightarrow {}^1B_{1g}$
	23,300	257	$^1A_{1g} \rightarrow {}^1E_g$[a]
DMF + KCN	13,600	56	$^1A_{1g} \rightarrow {}^1A_{2g}$
	20,400	132	$^1A_{1g} \rightarrow {}^1B_{1g}$
	22,300	242	$^1A_{1g} \rightarrow {}^1E_g$[a]

[a] Questionable assignment.

species have their first absorption maximum at higher energies than the comparable bisdithiolate complex. This is consistent with previously reported complexes of this type.[2]

One further point is worthy of note. The substitution of bromine on the carborane nucleus in carboranedithiolate species appears to have some effect on the strength of complexation as indicated by the variation in the respective Δ_1 values. The same type of alteration was not observed in the phosphinocarboranes.

TABLE IV

LIGAND FIELD SPECTRAL DATA

Complex[a,b]	λ_{max}, cm^{-1}	Δ_1, cm^{-1} [c]
$[(C_2H_5)_4N]_2[Ni(DMC)_2]$	13,900	16,690
	20,400	
	23,250	
$[((C_6H_5)_3P)_2Ni(DMC)]$	16,500	19,330
	20,000	
$[((C_6H_5)_3P)_2Ni(DMMBC)]$	18,500	21,320
$[(TPP)Ni(DMC)]$	22,200[d]	
$[(DPPC)Ni(DMC)]$	20,400	23,210
	22,200[d]	
$[Ni(DPPC)_2]Cl_2$	21,500[d]	
$[(DPPC)NiCl_2]$	17,850 sh	20,660
	20,200[d]	
	21,700[d]	
$[Ni(DPMBC)_2]Cl_2$	20,800[d,e]	
	22,700[d]	
$[Ni(DPDBC)_2]Cl_2$	21,300 (ε 1640)[d,f,g]	
$[Ni(DPTBC)_2]Cl_2$	21,300 (ε 3200)[d,f,g]	

[a] Abbreviations listed in Table I. [b] Spectra obtained on Nujol mulls unless otherwise specified. [c] Δ_1 values calculated using the relationship $F_2 = 10F_4 = 800$ cm^{-1}. [d] The absorption due entirely, or in part, to a charge-transfer phenomenon. [e] Spectrum was also obtained in DMF. One absorption at 21277 cm^{-1} (ε 2600) was noted. This absorption arises from a charge-transfer phenomenon. [f] Spectra obtained in DMF. [g] DPDBC = 1,2-bis(diphenylphosphino)dibromo-o-carborane and DPTBC = 1,2-bis(diphenylphosphino)tribromo-o-carborane.

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Circular Dichroism of the Tris[di-μ-hydroxo-bis(ethylenediamine)cobalt(III)]cobalt(III) Ion

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The results and implications of the fractional precipitation of tris[di-μ-hydroxo-bis(ethylenediamine)cobalt(III)]cobalt(III) nitrate with potassium *d*-antimonyltartrate are reported and the kinetic behavior of the fractions is used to determine their purity. It appears that only four of the eight possible isomers are formed in the synthesis of the complex ion and that only two of these are resolved under the experimental conditions. The circular dichroism is discussed in terms of four adjacent but relatively noninteracting chromophores. However, it is shown that it is impossible to assign uniquely the absolute configurations of the central and peripheral octahedra on the bases of the signs of the rotational strengths from the dominant dichroism maxima.

Werner's[1] polynuclear compound, tris[di-μ-hydroxo-bis(ethylenediamine)cobalt(III)]cobalt(III) nitrate, was only recently resolved by Goodwin, Gyarfas, and Mellor.[2] Of the eight isomers having Werner's proposed structure it was believed that four were obtained by fractional precipitation with *d*- and *l*-antimonyltartrate and subsequent conversion to their thiocyanates. The distinct differences between the four, which were designated as D_I, L_I, D_{II}, and L_{II} and thought to consist of two enantiomeric pairs, were established by their specific rotations and their rates of racemization: $[\alpha]^{20}_D$ ±3920° and $t_{1/2} = 1.9$ hr (40°) for D_I and L_I, while $[\alpha]^{20}_D$ ±3620° and $t_{1/2} = 19$ hr (40°) for D_{II} and

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[1] A. Werner, *Ber.*, **40**, 2103 (1907).

[2] H. A. Goodwin, E. C. Gyarfas, and D. P. Mellor, *Australian J. Chem.*, **11**, 426 (1958).