

general agreement with Tolman's work on nickel(0)-phosphine complexes²⁶ and may facilitate the design of d¹⁰ complexes containing tertiary group V donor ligands as specific catalysts.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BROOKLYN COLLEGE OF THE CITY UNIVERSITY OF NEW YORK, BROOKLYN, NEW YORK 11210

N-Aralkylpolyamine Complexes. II.¹ Five- and Six-Coordinate Complexes of Copper(II) with *N,N'*-Dibenzylethylenediamine

BY K. C. PATEL* AND DAVID E. GOLDBERG

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The preparation and characterization of [Cu(DBen)₂Br]ClO₄, [Cu(DBen)₂(NCS)(NO₃)], [Cu(DBen)₂(SeCN)(NO₃)], [Cu(DBen)₂(SeCN)(ClO₄)], [Cu(DBen)₂(SCN)]Br, and [Cu₂(DBen)₄(SCN)(ClO₄)₂]ClO₄ are reported. [Cu(DBen)₂Br]Br was also characterized. Reflectance spectra at room temperature and at liquid nitrogen temperature, magnetic susceptibilities from room temperature to liquid nitrogen temperature, infrared and far-infrared spectra, and visible spectra and molar conductivities in DMF and methanol were used to deduce the structures. Preliminary electron spin resonance spectra of some of the complexes are also reported. Most noteworthy is the existence of the [Cu(DBen)₂Br]⁺ cation in both trigonal-bipyramidal and square-pyramidal forms.

Introduction

Ethylenediamine and *N*-alkylethylenediamines are well known for their high coordinating abilities, but little is known of *N*-aralkylethylenediamines. There is one description of the electronic and magnetic properties of some copper(II) dibenzylethylenediamine (DBen) complexes.¹ According to the method of preparation, the Cu(DBen)₂Br₂ complex can be isolated in two geometric forms—a five-coordinate form and a tetragonal form.¹ There are two reports on stability constants of DBen complexes,^{2,3} and further stability constant work, in dilute solution, has recently been completed.⁴ Ni(DBen)₂Br₂ exists as a five-coordinate complex.⁵

There has recently been great interest in the bonding of the thiocyanate ligand to metal ions.⁶ Jørgensen⁷ has suggested that a given metal ion in either high or low oxidation state may exhibit M–SCN bonding, whereas in an intermediate oxidation state, the bond type may be M–NCS. Until Brown and Lingafelter⁸ showed from X-ray analysis that the thiocyanate ligand is S bonded to copper in the Cu(en)₂(SCN)₂ complex, it was commonly believed that all of the thiocyanate complexes of first transition series metals are N bonded. Basolo, *et al.*,⁹ have shown that Pd–NCS bonding occurs in [Pd(Et₄dien)(NCS)]⁺, while Pd–SCN bonding occurs in [Pd(dien)(SCN)]⁺, a difference which was considered to result from the steric factors and the differing basicities of the amines. At present, the thiocyanate ligand is known to bond in five different

ways:¹⁰ MSCN, MNCS, MSCNM, M₂SCN, and M₂SCNM. The selenocyanate ligand is also known to bond through either its nitrogen atom, its selenium atom, or both.

Experimental Section

Copper(II) salts (reagent grade), potassium selenocyanate (K & K Laboratories), and dibenzylethylenediamine (Aldrich Chemical Co.) were used without further purification. Spectro Grade solvents were used for solution spectra and for conductance measurements. Analytical data are presented in Table I.

Diffuse reflectance spectra at room temperature and at liquid nitrogen temperature were recorded on a Cary Model 14 spectrophotometer equipped with a diffuse reflectance accessory using magnesium oxide as reference. Solution spectra were recorded on the same instrument, using 1-cm silica cells and 10⁻³ M solutions.

Molar conductances of the 10⁻³ M solutions were determined at 25° using a Wayne Kerr Universal conductivity bridge, Model B221. Infrared spectra of Nujol or hexachlorobutadiene mulls were recorded between KBr plates over the range 5000–650 cm⁻¹ with a Perkin-Elmer Model 21 spectrophotometer. The far-infrared spectra were measured between polyethylene plates over the range 600–250 cm⁻¹ on a Perkin-Elmer Model 457 spectrophotometer. They and the magnetic susceptibility measurements were done on a Gouy balance at the University of Surrey, Guildford, Surrey, England. The esr spectra were recorded at Hunter College of the City University of New York on a Varian V4502 spectrometer.

(I) **Bromobis(*N,N'*-dibenzylethylenediamine)copper(II) Perchlorate.**—[Cu(DBen)₂Br]Br was prepared from aqueous solution.¹ To a suspension of this compound (0.01 mol) in absolute ethanol was added solid LiClO₄ (0.012 mol). The solids were dissolved by heating at 95°. The resulting filtrate yielded navy blue crystals, which were washed with absolute ethanol.

(II) **Isothiocyanatonitratobis(*N,N'*-dibenzylethylenediamine)copper(II).**—A suspension of Cu(DBen)₂(NO₃)₂ (0.01 mol), prepared as described previously,¹ in absolute ethanol was treated with solid NH₄SCN (0.01 mol). The pink solid turned blue on shaking the mixture. The product was filtered and washed with ethanol. Recrystallization from DMF is not possible because of its very high solubility, but ethanol or a mixture of DMF and ethanol yields solid Cu(DBen)₂(NO₃)₂.

(III) **Selenocyanatonitratobis(*N,N'*-dibenzylethylenediamine)-**

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TABLE I
ELEMENTAL ANALYSES^a

Compd and color	% C		% H		% N		% S		% Se ^b	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
[Cu(DBen) ₂ Br]ClO ₄ (navy blue)	53.1	53.1	5.6	5.9	7.7	7.8				
[Cu(DBen) ₂ (NCS)(NO ₃)] (blue)	59.7	59.1	6.05	6.0	12.65	12.4	4.8	5.05		
[Cu(DBen) ₂ (SeCN)(NO ₃)] (dirty blue)	55.7	54.9	5.7	5.8	11.8	12.1			11.1	11.2
[Cu(DBen) ₂ (SeCN)(ClO ₄)] (greenish blue)	52.9	52.7 50.9	5.35	5.3 5.2	9.4	10.2 9.7			10.6	10.2 10.3
[Cu(DBen) ₂ (SCN)]Br (green)	58.1	56.7	5.9	6.2	10.3	10.5	4.7	4.7		
[Cu ₂ (DBen) ₄ (SCN)(ClO ₄) ₂]- ClO ₄ ^c (blue)	54.05	53.3 53.2	5.5	6.35 5.65	8.7	8.9 9.2	2.2	2.3 2.2		

^a Microanalyses by Alfred Bernhardt Microanalytical Laboratory, Elbach über Engelskirchen, West Germany. ^b Microanalysis of selenium is difficult and was done by control analysis. ^c Prepared by treating Cu(DBen)₂(ClO₄)₂·H₂O and NH₄SCN in the mole ratios 1:1 and 1:2, respectively.

TABLE II
MAGNETIC PROPERTIES, MOLAR CONDUCTANCES (Λ_M), AND FREQUENCIES OF INFRARED BANDS DUE TO SCN OR SeCN OF Cu(II)-DBen COMPLEXES

Complex	μ_{eff}^a , BM		θ , °K	Diamag cor $\times 10^6$, cgsu	Λ_M , cm ² /mol ohm		C-N str, cm ⁻¹
	300°K	90°K			DMF	CH ₃ OH	
[Cu(DBen) ₂ Br]ClO ₄	1.98	1.90	10	441	81	106	...
[Cu(DBen) ₂ (NCS)(NO ₃)]	1.92	1.89	5	424	88	89	2096
[Cu(DBen) ₂ (SeCN)(NO ₃)]	2.11	1.96	13	435	103	92	2042, 2060 w, sh, 2080 w, sh, 2100 w, sh
[Cu(DBen) ₂ (SeCN)(ClO ₄)]	1.86	1.79	14	448	118	<i>b</i>	2050, 2090 sh
[Cu(DBen) ₂ (SCN)]Br	1.90	440	6	72	2065
[Cu ₂ (DBen) ₄ (SCN)(ClO ₄) ₂]ClO ₄	1.94	1.80	...	438	57 ^c	<i>b</i>	2050

^a Calculated, using the relationship $\mu_{\text{eff}} = 2.84\sqrt{\chi_A T}$ BM; χ_A is the molar susceptibility corrected for the diamagnetism of the ligands and anions. ^b Insufficient solubility. ^c Assuming a formula weight of 722, corresponding to a monomeric formula.

copper(II).—To a suspension of Cu(DBen)₂(NO₃)₂ (0.01 mol) in absolute ethanol was added KSeCN (0.01 mol). Reaction took place immediately, producing a dirty blue solid, which was washed with ethanol, then with water, and finally once again with ethanol. It was impossible to prepare Cu(DBen)₂(SeCN)₂ from Cu(SeCN)₂, since the latter is unstable even in absolute ethanol, decomposing into CuSe.

(IV) Selenocyanatoperchloratobis(*N,N'*-dibenzylethylenediamine)copper(II).—A suspension in absolute ethanol of Cu(DBen)₂(ClO₄)₂·H₂O (0.01 mol), prepared as described previously,¹ was treated with a solution of KSeCN (0.01 mol) in absolute ethanol. The resulting greenish blue solid was filtered, washed with ethanol, and dried. The dry solid was washed with water to ensure removal of all traces of KSeCN and then was washed with ethanol.

(V) Thiocyanatobis(*N,N'*-dibenzylethylenediamine)copper(II) Bromide.—To a suspension of [Cu(DBen)₂Br]Br (0.01 mol) in absolute ethanol was added solid NH₄SCN (0.01 mol). The solids were dissolved by heating. From the filtered blue solution, blue crystals separated and were filtered and washed with absolute ethanol.

(VI) Thiocyanatobis(perchlorato)tetrakis(*N,N'*-dibenzylethylenediamine)dicationicopper(II) Perchlorate.—A solution of NH₄SCN (0.01 or 0.02 mol) in absolute ethanol was treated with a suspension of Cu(DBen)₂(ClO₄)₂·H₂O¹ (0.01 mol) in the same solvent. The resulting blue solid was filtered, washed with ethanol, and dried.

Results and Discussion

Six new coordination compounds of DBen with copper(II) have been prepared, and their reflectance spectra have been measured both at room temperature and at liquid nitrogen temperature. Magnetic susceptibilities from room temperature down to liquid nitrogen temperature, infrared and far-infrared spectra, and visible spectra and molar conductivities in DMF and methanol are reported in Tables II and III. The

infrared spectra between 600 and 250 cm⁻¹ are very complicated (Table IV); however, assignments of certain bands are made by mutual comparison and by comparison with literature values. The magnetic susceptibilities are discussed as a group, after which the other properties of each compound are discussed, and finally esr spectra are discussed.

Magnetic Susceptibilities.—Magnetic susceptibilities were measured at seven temperatures between 87.5 and 300°K. The magnetic moments at 300 and 90°K and the Curie-Weiss constants of all the complexes are reported in Table II. The compounds are all magnetically normal, high-spin copper(II) complexes except Cu₂(DBen)₄SCN(ClO₄)₃, which may show a weak anti-ferromagnetic interaction.

[Cu(DBen)₂Br]ClO₄.—From their spectral and other properties, two isomers of Cu(DBen)₂Br₂—a blue complex prepared from ethanolic solution and a dark blue complex prepared from aqueous solution—have been assigned tetragonal and five-coordinate structures, respectively.¹ To characterize the five-coordinate complex further, a dark navy blue complex has now been isolated by replacement of a bromide ion by perchlorate. The reflectance spectra of all three complexes differ, as shown in Figure 1. The tetragonal form of Cu(DBen)₂Br₂ has a band in its reflectance spectrum at 14,500 cm⁻¹, with a shoulder near 10,200 cm⁻¹. The five-coordinate form of the dibromide has a very broad band at 12,600 cm⁻¹. The reflectance spectrum of the perchlorate has an intense band at 17,000 cm⁻¹ and an unresolved shoulder near 15,000 cm⁻¹ (Table III). The reflectance spectrum of a complex reflects the energy

TABLE III
ELECTRONIC SPECTRA OF Cu(II)-DBen COMPLEXES

	Reflectance spectra, ^a kK		Soln spectra, kK (ε)	
	Room temp	Liq N ₂ temp	DMF	Methanol
[Cu(DBen) ₂ Br]ClO ₄	17.0 ~15.0 vw, sh	17.0 ~15.0 vw, sh	14.65 ^b (255)	15.6 ^b (160)
[Cu(DBen) ₂ (NCS)(NO ₃)]	14.5 11.1	14.8 10.6	27.3 sh (820) 15.5 ^b (185)	28.6 (1100) 15.4 ^b (180)
[Cu(DBen) ₂ (SeCN)(NO ₃)]	16.2 11.5 sh	16.5 11.8 sh	25.5 (160) 16.7 ^b (165)	28.6, 27.0 (400) 15.6 ^b (80)
[Cu(DBen) ₂ (SeCN)(ClO ₄)]	16.2 11.5 sh	16.7 11.5 sh	25.0 (250) 16.0 (160)	<i>c</i>
[Cu(DBen) ₂ (SCN)]Br	14.7 ~12.0 vw, sh	14.9 ~11.0 sh	14.7 ^b (238)	27.8 sh (1000) 15.5 ^b (195)
[Cu ₂ (DBen) ₄ (SCN)(ClO ₄) ₂]ClO ₄	16.6 11.3 sh	16.8 11.8 sh	25.0 (250) 16.0 (160)	<i>c</i>

^a All bands are broad. ^b Asymmetric on the low-energy side. ^c Insufficient solubility.

TABLE IV^a
INFRARED SPECTRA OF NUJOL MULLS OF Cu(II)-DBen COMPLEXES BETWEEN 600 AND 250 CM⁻¹

[Cu(DBen) ₂ Br]ClO ₄	[Cu(DBen) ₂ (NCS)(NO ₃)]	[Cu(DBen) ₂ (SeCN)(NO ₃)]	[Cu(DBen) ₂ (SeCN)(ClO ₄)]	[Cu(DBen) ₂ (SCN)]Br	[Cu ₂ (DBen) ₄ (SCN)(ClO ₄) ₂]ClO ₄	[Cu(DBen) ₂ Br]Br
585 m	581 m	580 m	578 m	585 s	582 m	{580 s}
570 w	560 w	550 vw	550 w	503 m	550 w, br	{570 m}
{512} s	510 m	510 s	509 s	483 w	511 m	{508 m}
{508} s	492 m	500 s	498 s		499 m	{497 s}
498 m						
457 s	460 s	456 sh	465 vw, sh	{465}	487 w	460 s
410 s	{425 w}	448 s	446 s	{460} s	478 w	437 w
	{410 m}	425 m	420 s	405 sh	468 w	{410}
	395 m			392 m	450 s	{407} m
					425 s	
380 vw	365 m	378 w	378 w	370 w	380 w	360 w
330 w	340 w, br, 318 w	320 w	350 vw	332 w	350 vw, br	337 w
300 w, sh	297 w, sh	297 s	323 w		327 w	
			295 s		300 s, br	
280 s	283 w, sh 272 m	270 m	270 m	272 m	270 m	280 vw, sh 260 s, br

^a Braces indicate split bands.

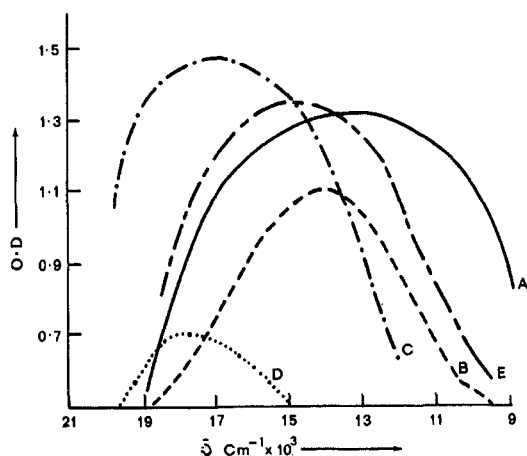


Figure 1.—Diffuse reflectance spectra at room temperature of [Cu(DBen)₂Br]Br (A), [Cu(DBen)₂Br₂] (B), [Cu(DBen)₂Br]ClO₄ (C), [Cu(DBen)₂](ClO₄)₂·H₂O (D), and [Cu(DBen)₂(SCN)]Br (E).

levels of the cation, which are controlled largely by the nature of the donor atoms and the local symmetry about the metal ion. The great differences in the spectra of these three compounds cannot be caused by a difference in (uncoordinated) anion. Many cationic complexes are known in which the anions have very little effect on the reflectance spectrum of the compound,¹¹⁻¹³ and hence the cations are assigned identi-

cal structures in these cases. Nor is it possible for ligand conformation to cause such appreciable changes, although such isomerism has caused changes in the colors of certain complexes with the same local symmetry.¹⁴ Considering all these factors, it is reasonable to believe that Cu(DBen)₂BrClO₄ and the two forms of Cu(DBen)₂Br₂ must all have different structures.

Cu(DBen)₂BrClO₄ has a strong, broad infrared band near 1100 cm⁻¹, characteristic of an ionic perchlorate group (Figure 2). The expected band near 630 cm⁻¹ is masked by ligand vibrations. With the perchlorate ionic, the possible structures for the cation are square planar, with only DBen coordinated, or some five-coordinate complex with DBen and bromide ion coordinated. The former can be eliminated as a possibility by comparison of the reflectance spectrum of this complex with that of a square-planar complex,¹ Cu(DBen)₂(ClO₄)₂·H₂O (Figure 1). The reflectance band of the Cu(DBen)₂BrClO₄ complex is much more intense and is shifted 700 cm⁻¹ toward low energy compared with that of Cu(DBen)₂(ClO₄)₂·H₂O, which resembles the change in electronic spectrum¹⁵ that occurs between [Cu(en)₂]X₂ and [Cu(en)₂(NH₃)]X₂ and with the "pentaammine effect" observed¹⁶ in aqueous solutions of copper(II) ion as ammonia is added. Such a high increase in intensity of a d-d reflectance band suggests

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Figure 2.—Infrared spectra of $[\text{Cu}(\text{DBen})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (A), $[\text{Cu}(\text{DBen})_2\text{Br}]\text{ClO}_4$ (B), and $[\text{Cu}_2(\text{DBen})_4(\text{SCN})(\text{ClO}_4)_2]\text{ClO}_4$ (C).

a loss of center of symmetry. Far-infrared bands at 280 cm^{-1} of $\text{Cu}(\text{DBen})_2\text{BrClO}_4$ and at 260 cm^{-1} with a weak shoulder at 280 cm^{-1} of $\text{Cu}(\text{DBen})_2\text{Br}_2$, which are much stronger and broader than bands in the same region for the other complexes, possibly includes a band due to metal–bromine stretch (Table IV). From these results, a five-coordinate structure is assigned to $[\text{Cu}(\text{DBen})_2\text{Br}]\text{ClO}_4$. Hence it is believed that the five-coordinate cation $[\text{Cu}(\text{DBen})_2\text{Br}]^+$ exists in two isomeric forms, in $[\text{Cu}(\text{DBen})_2\text{Br}]\text{Br}$ and $[\text{Cu}(\text{DBen})_2\text{Br}]\text{ClO}_4$.

A square-pyramidal structure is assigned to the cation of $[\text{Cu}(\text{DBen})_2\text{Br}]\text{ClO}_4$ and a trigonal-bipyramidal structure is assigned to the cation of $[\text{Cu}(\text{DBen})_2\text{Br}]\text{Br}$ on the basis of the following comparisons. The reflectance spectrum of a square-pyramidal complex, $[\text{Cu}(\text{trien})(\text{SCN})]\text{NCS}$, whose structure was determined by X-ray diffraction,¹⁷ has a broad asymmetric band at $17,400\text{ cm}^{-1}$. Also the members of a series of bis(ethylenediamine)copper(II)–monoammonia complexes were assigned square-pyramidal structures¹⁵ from their reflectance spectra, each of which has an intense band at $17,000\text{ cm}^{-1}$ with a very weak shoulder near $11,000\text{ cm}^{-1}$. In contrast, the reflectance spectrum of $\text{Cu}(\text{NH}_3)_2\text{Ag}(\text{SCN})_3$, which has been assigned a regular trigonal-bipyramidal structure from X-ray analysis,¹⁸ has two strong, broad bands of high intensity at $12,800$ and $14,500\text{ cm}^{-1}$ (which appear almost as a single band). $\text{Cu}(\text{dienMe})\text{Cl}_2$, $\text{Cu}(\text{dienMe})\text{Br}_2$, $[\text{Cu}(\text{bipy})_2\text{NH}_3](\text{ClO}_4)_2$, and $[\text{Cu}(\text{bipy})_2\text{NH}_3](\text{BF}_4)_2$, with electronic properties very similar to those of $\text{Cu}(\text{NH}_3)_2\text{Ag}(\text{SCN})_3$, were assigned^{19,20} trigonal-bipyramidal structures. Using these results as guides, a square-pyramidal and a trigonal-bipyramidal structure can be assigned to $[\text{Cu}(\text{DBen})_2\text{Br}]\text{ClO}_4$ and $[\text{Cu}(\text{DBen})_2\text{Br}]\text{Br}$, respectively. These results are consistent with the esr spectra (see esr section). Square-planar, octahedral, and tetrahedral isomers are well established for nickel-

(II) complexes.²¹ Recently diamagnetic and paramagnetic forms of $\text{Ni}(\text{DBen})_2(\text{ClO}_4)_2$ were isolated.⁵ However, to our knowledge, the present report is the first report of structural isomerism in a five-coordinate copper(II) cation.

$[\text{Cu}(\text{DBen})_2\text{Br}]\text{ClO}_4$ behaves as a uni-univalent electrolyte²² in DMF. The spectrum in this solvent consists of one broad band at $14,650\text{ cm}^{-1}$, a frequency much different from that in the reflectance band.

$[\text{Cu}(\text{DBen})_2(\text{NCS})(\text{NO}_3)]$, $[\text{Cu}(\text{DBen})_2(\text{SeCN})(\text{NO}_3)]$, and $[\text{Cu}(\text{DBen})_2(\text{SeCN})(\text{ClO}_4)]$.—The reflectance bands at $14,500$ and $11,100\text{ cm}^{-1}$ of $[\text{Cu}(\text{DBen})_2(\text{NCS})(\text{NO}_3)]$ and at $16,200$ and $11,500\text{ cm}^{-1}$ of both $[\text{Cu}(\text{DBen})_2(\text{SeCN})(\text{NO}_3)]$ and $[\text{Cu}(\text{DBen})_2(\text{SeCN})(\text{ClO}_4)]$ are characteristic of distorted octahedral (C_{4v}) coordination. In this symmetry three bands are expected.²³ The broad high-energy band (main band) can be assigned to the superimposed transitions ${}^2B_1 \rightarrow {}^2B_2$ and ${}^2B_1 \rightarrow {}^2E$ and the other band or shoulder to the ${}^2B_1 \rightarrow {}^2A_1$ transition. Comparison of the low-energy bands (distortion bands) of $[\text{Cu}(\text{DBen})_2(\text{NCS})(\text{NO}_3)]$ and $[\text{Cu}(\text{DBen})_2(\text{SeCN})(\text{NO}_3)]$ clearly indicates (by the shift of the band toward lower energy in the former) lower distortion in the former complex, as expected¹ (Figure 3). As noted earlier²⁴ for $\text{Cr}(\text{en})_2\text{X}_2$ complexes ($X =$

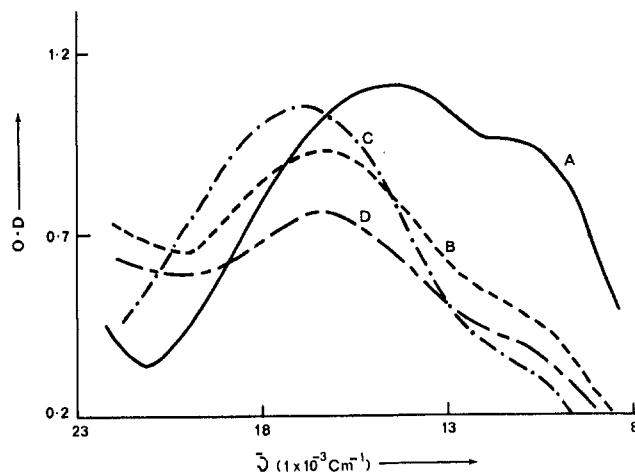


Figure 3.—Diffuse reflectance spectra at room temperature of $[\text{Cu}(\text{DBen})_2(\text{NCS})(\text{NO}_3)]$ (A), $[\text{Cu}(\text{DBen})_2(\text{SeCN})(\text{NO}_3)]$ (B), $[\text{Cu}_2(\text{DBen})_4(\text{SCN})(\text{ClO}_4)_2]\text{ClO}_4$ (C), and $[\text{Cu}(\text{DBen})_2(\text{SCN})]\text{Br}$ (D).

Br or I), this type of band shift also indicates coordination of both anions. On cooling to liquid nitrogen temperature, the main band in all three complexes moved $300\text{--}500\text{ cm}^{-1}$ higher in energy, as expected for a d–d transition.

The conductance and spectral data in methanol and DMF are reported in Tables II and III, respectively. In these solvents $[\text{Cu}(\text{DBen})_2(\text{NCS})(\text{NO}_3)]$ behaves as a uni-univalent electrolyte and absorbs near $15,500\text{ cm}^{-1}$. $[\text{Cu}(\text{DBen})_2(\text{SeCN})(\text{NO}_3)]$ decomposes slowly in methanol.

The coordination of both anions in the solid com-

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plexes is confirmed from the infrared spectra. The presence of infrared bands (in cm^{-1}) at 824 (m) (ν_2) and 1305 (s) and 1400 (s) (ν_3) confirms the monodentate coordination of the nitrate group in both nitrate complexes.²⁵ The two bands at ~ 318 and at 297 cm^{-1} can be assigned to M-O stretching modes of mono-coordinated nitrate groups²⁶ (Table IV).

The weak splitting of an infrared band between 1050 and 1100 cm^{-1} in $[\text{Cu}(\text{DBen})_2(\text{SeCN})(\text{ClO}_4)]$ can be assigned to semicoordinated²⁷ perchlorate ion. The presence of far-infrared bands at 323 (w) and 295 (s) cm^{-1} due to Cu-O bonding, as well as a shoulder at 465 cm^{-1} , due to the ν_2 vibration of the ClO_4 group, also supports this assignment (Table IV). (See also the discussion of $[\text{Cu}_2(\text{DBen})_4(\text{SCN})(\text{ClO}_4)_2](\text{ClO}_4)$.)

The thiocyanate ion has three fundamental modes of vibration—the C-N stretch, ν_1 ; the doubly degenerate bending, ν_2 ; and the C-S stretch, ν_3 . The C-N stretching frequencies of N-bonded, S-bonded, SCN-bridged, and $>\text{SC}\equiv\text{N}$ -triply coordinated thiocyanate groups occur between 2040 and 2080, 2080 and 2120, 2119 and 2133, and 2140 and 2170 cm^{-1} , respectively.⁶ Therefore the ν_1 band at 2096 cm^{-1} of $[\text{Cu}(\text{DBen})_2(\text{NCS})(\text{NO}_3)]$ characterizes an S-bonded thiocyanate group. However, contrary to this assignment, bands between 2070 and 2100 cm^{-1} in $\text{M}_2\text{M}'_2[\text{Zn}(\text{NCS})_6] \cdot n\text{H}_2\text{O}$ complexes (where M and M' are Na, K, Cs, and NH_4) and also a band at 2073 cm^{-1} in $[\text{Cu}(\text{trien})\text{SCN}](\text{NCS})$ have been assigned to N-bonded²⁸ and S-bonded¹⁷ SCN groups, respectively.

The region of C-S stretching frequency has been suggested as $780\text{--}860 \text{ cm}^{-1}$ in N-bonded complexes and $690\text{--}720 \text{ cm}^{-1}$ in S-bonded thiocyanate complexes.²⁹ In the series of complexes reported here, this region cannot be used confidently because the substituted aromatic ring vibrations occur here. However, the ν_3 band of $[\text{Cu}(\text{DBen})_2(\text{NCS})(\text{NO}_3)]$ at 880 cm^{-1} , where neither NO_3 nor DBen absorbs, may suggest the presence of an N-bonded thiocyanate group. The differences in the C-N stretching bands of $[\text{Cu}(\text{DBen})_2(\text{SeCN})(\text{NO}_3)]$ and $[\text{Cu}(\text{DBen})_2(\text{NCS})(\text{NO}_3)]$ (Table II) suggests³⁰ that both compounds cannot be N coordinated. Also, bands between 2040 and 2080 cm^{-1} have been interpreted in terms of Se-bonded selenocyanatodiamine-copper(II) complexes.²⁹ Hence it is suggested that this complex contains a selenium-bonded SeCN group.

The C-N stretching vibration of the SeCN group of $[\text{Cu}(\text{DBen})_2(\text{SeCN})(\text{ClO}_4)]$ appears as a strong, sharp band at 2050 cm^{-1} with a shoulder near 2090 cm^{-1} (Table II). The appearance in the spectrum of a C-Se stretching band at 510 cm^{-1} and a doubly degenerate bending vibration at 378 cm^{-1} with its weak overtone at 762 cm^{-1} in both the SeCN complexes confirms the presence of a selenium-bonded SeCN group.³¹

$[\text{Cu}(\text{DBen})_2(\text{SCN})]\text{Br}$.—From the appearance of the reflectance spectrum, a highly distorted tetragonal structure or a square-pyramidal structure was considered most probable for this compound. But the

reflectance spectrum has an intense band at $14,700 \text{ cm}^{-1}$ with a weak shoulder near $12,000 \text{ cm}^{-1}$. From the absence of a band below $12,000 \text{ cm}^{-1}$, the distorted octahedral structure can be ruled out for the following reasons. A highly distorted tetragonal complex,¹ $\text{Cu}(\text{DBen})_2\text{I}_2$, has a distortion band at $10,600 \text{ cm}^{-1}$ in its reflectance spectrum. Because of the smaller atomic radii and higher ligating power of nitrogen or sulfur and bromide than of iodide, comparatively less distortion and hence a distortion band at energy lower than $10,600 \text{ cm}^{-1}$ could be expected in the spectrum of $\text{Cu}(\text{DBen})_2(\text{SCN})\text{Br}$ if it did have a tetragonal structure. The reflectance spectrum of this complex is comparable to that of the square-pyramidal complex¹⁷ $[\text{Cu}(\text{tpt})-(\text{NCS})]\text{NCS}$ (tpt = tris(3-aminopropyl)amine).

$[\text{Cu}(\text{DBen})_2(\text{SCN})]\text{Br}$ behaves as a uni-univalent electrolyte in methanol, and its solution spectrum has a band at $15,500 \text{ cm}^{-1}$. However, this compound is a nonelectrolyte in DMF and has a solution band at $14,700 \text{ cm}^{-1}$. The C-S stretching modes between 730 and 750 cm^{-1} are reported for weakly sulfur-bonded bis(diamine)copper(II) thiocyanate complexes.²⁹ The appearance of a band at 743 cm^{-1} in addition to a normal band in this region of a substituted benzene ring can be assigned to a weakly sulfur-bonded thiocyanate group.²² Absence of a band between 260 and 280 cm^{-1} of a coordinated bromide ion confirms the presence of an ionic bromide ion.

$\text{Cu}_2(\text{DBen})_4(\text{SCN})(\text{ClO}_4)_3$.—Treatment of $\text{Cu}(\text{DBen})_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ with NH_4SCN in a molar ratio of 1 or 2 in cold ethanol yields a light blue solid which analyzes as $\text{Cu}_2(\text{DBen})_4(\text{SCN})(\text{ClO}_4)_3$ (Table I). The reflectance spectrum of this complex has a broad band at $16,600 \text{ cm}^{-1}$ and a weak shoulder near $11,300 \text{ cm}^{-1}$, which can be interpreted in terms of a tetragonal complex.

This compound behaves as a tri-univalent electrolyte in DMF solution,²² and its spectrum has a single broad band at $16,000 \text{ cm}^{-1}$, which probably indicates some solvation (Table III).

Comparison of the infrared spectra of $[\text{Cu}(\text{DBen})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, $[\text{Cu}(\text{DBen})_2\text{Br}]\text{ClO}_4$, and $\text{Cu}_2(\text{DBen})_4(\text{SCN})(\text{ClO}_4)_3$ in the $1100\text{--}\text{cm}^{-1}$ region clearly indicates the presence of both ionic and monodentate perchlorate groups²⁷ in $\text{Cu}_2(\text{DBen})_4(\text{SCN})(\text{ClO}_4)_3$ (Figure 2). The ratio of band intensities of ν_1 and ν_3 was used as evidence to show coordination of the perchlorate group.²⁷ The intensity ratios for $\text{Cu}(\text{DBen})_2(\text{SeCN})(\text{ClO}_4)$, 37, and for $\text{Cu}_2(\text{DBen})_4(\text{SCN})(\text{ClO}_4)_3$, 40, in contrast to those for $\text{Cu}(\text{DBen})_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, 19, and for $[\text{Cu}(\text{DBen})_2\text{Br}]\text{ClO}_4$, 20, indicate that semicoordination of ClO_4^- has taken place in the first two complexes. The appearance of a ν_2 band at $468 \text{ (w)} \text{ cm}^{-1}$ also suggests the presence of a semicoordinated perchlorate group.

The C-N stretching band of the thiocyanate group appears at 2050 cm^{-1} , where the ionic thiocyanate group absorbs. However, bands at 300 cm^{-1} and at 425 cm^{-1} can be assigned to M-S stretching and SCN bending vibrations, respectively,³² of a sulfur-bonded SCN group. Moreover, the presence of 0.5 mol of thiocyanate per mole of copper from both preparations suggests that the role of the thiocyanate must be more than just an anion in this complex. Hence, despite

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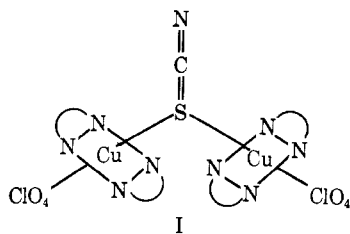
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many reports⁶ that the C-N stretching vibration of a bridging thiocyanate group occurs above 2100 cm⁻¹, structure I is postulated. Recently this type of bonding has been confirmed by X-ray analysis in [Pd(SCN)₄]²⁻.



Electron Spin Resonance Spectra.—Electron spin resonance spectra of polycrystalline samples of some copper(II) complexes are presented in Figure 4. The esr spectrum of [Cu(DBen)₂Br]ClO₄ is isotropic, with a *g* value of 2.16, consistent with a square-pyramidal structure undergoing free rotation, such as that observed²³ in Cu(NH₃)₆(BF₄)₂ (*g* = 2.126).

The esr spectrum of [Cu(DBen)₂Br]Br is anisotropic, with *g* values of 2.034, 2.074, and 2.203, consistent with a distorted trigonal-bipyramidal structure with a *d*₂ ground state. From the nature of the spectrum, the distortion in this complex seems opposite to that³³ in [Cu(bipy)₂I]I, which may reflect the rigidity of bipyridine as opposed to the flexibility of DBen.

The esr spectrum of [Cu(DBen)₂(NCS)(NO₃)] is

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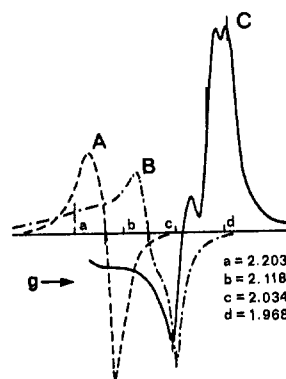


Figure 4.—The powder esr spectra (first derivative) of [Cu(DBen)₂Br]ClO₄ (A), [Cu(DBen)₂Br]Br (B), and [Cu(DBen)₂(NCS)(NO₃)] (C).

highly anisotropic. The average *g* value in an anisotropic system can be calculated using the relation³⁴

$$g_{av} = \sqrt{g_{\parallel}^{2/3} + 2g_{\perp}^{2/3}} \quad (1)$$

where $g_{\parallel} = g_z$ and $g_{\perp} = (g_x + g_y)/2$. Using the values $g_{\parallel} = 2.036$ and $g_{\perp} = (g_x + g_y)/2 = 1.981$ in the present case, the value $g_{av} = 2.000$ can be obtained.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA, CHAPEL HILL, NORTH CAROLINA 27514

The Magnetism of Substituted Quinoxaline Complexes of Copper(II)

BY GUY W. INMAN, JR., JAMES A. BARNES, AND WILLIAM E. HATFIELD*

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The magnetic susceptibilities of dichloro(2,3-dimethylquinoxalinato)copper(II) and dichlorobis(2-methylquinoxalinato)copper(II) have been measured over the temperature range 4.2–77°K and show maxima indicating an antiferromagnetic alignment of spins. The experimental data can best be fitted by the Ising model for an infinite linear chain, supporting past structure proposals that these compounds have polymeric structures. The values of the coupling constants are also consistent with chloride bridges in the 2-methyl complex and quinoxaline bridges in the 2,3-dimethyl complex. The magnetic data for dichlorobis(2,3-diphenylquinoxalinato)copper(II) show Curie-Weiss behavior down to very low temperatures where a small deviation indicative of a weak ferromagnetic interaction is observed.

Quinoxaline complexes of copper(II) halides were first prepared by Underhill.¹ On the basis of infrared and magnetic properties he proposed a polymeric structure for these compounds involving an infinite chain of CuX₂ units with quinoxaline molecules as bridges between copper atoms in different chains. Later work by Billing, *et al.*,² showed that the nature of the polymeric linkages was dependent on the degree and type of substitution on the quinoxaline ring. Their structural proposals were based on room-temperature moments, molecular models, and reflectance and infrared spec-

tra. Campbell, *et al.*,³ measured the magnetic susceptibility of dichloro(2,3-dimethylquinoxalinato)copper(II) over the temperature range 80–300°K and were able to fit their data to the Ising model for antiferromagnetic chains, although they did not observe a maximum in the susceptibility *vs.* temperature curves. To provide additional information bearing on the structures and properties of these compounds, we have measured the susceptibilities of dichloro(2,3-dimethylquinoxalinato)copper(II), dichlorobis(2,3-diphenylquinoxalinato)copper(II), and dichlorobis(2-methylquin-

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