

Figure 5. Variation of the entropies of complexation, ΔS_{101} and ΔS_{101}^* , of Sm(III) with various $(\text{CH}_2)_n(\text{CO}_2^-)_2$ ligands ($n = 0-4$). The values of ΔS_{102} and ΔS_{102}^* for the diacetate complexation are also included.

reflects the increasing loss of configurational entropy in the alkyl chain. The ΔS_{101}^* value for SmCHDCA^+ formation is more positive than for the adipate complex, even though both form nine-membered rings. Presumably, the CHDCA is in the boat form, which gives a more favorable configuration for chelation. The ΔS_{101}^* for $\text{Sm}(\text{OAc})_2$ formation is comparable to the glu-

tarate complexation value. We would expect that the ΔS_{101}^* values would have a "cratic" contribution¹¹ compared to the diacetate reaction of about $-33 \text{ J K}^{-1} \text{ mol}^{-1}$. If this is added to the ΔS_{101}^* values, the ΔS_{102}^* for $\text{Sm}(\text{OAc})_2^+$ becomes comparable to ΔS_{101}^* for SmSu^+ ($-78 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$). Apparently, the loss of configurational entropy in the succinate complex is about equal to the cratic entropy to which the primary stabilizing effect of chelation has been attributed.¹²

In summary, the complexation of lanthanide cations by alkanedicarboxylate ligands seems best described in terms of chelation even when the ring has nine members. The complexation stability decreases sharply as the ring size increases from five to seven, after which it shows much less effect of increasing ring size. The loss of configurational entropy in the chelated alkyl chain is a significant factor in the decreasing stability. In the cyclohexane ligand, CHDCA, the loss of configurational entropy in the nine-membered ring is less than in the adipate chelate, which is also a nine-membered ring. Presumably, the boat conformation of the CHDCA ligand is present in the complex, reducing strain in the chelate ring.

Acknowledgment. This research was supported through a contract with the USDOE, Office of Chemical Sciences.

- (11) Gurney, R. *Ionic Processes in Solution*; McGraw-Hill: New York, 1953.
 (12) Adamson, A. W. *J. Am. Chem. Soc.* **1954**, *76*, 1578.

Contribution from the National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China

Coordination of Thiocyanate in Tetraamine and Diimine-Diamine Complexes of Copper(II)

Der-Thin Wu and Chung-Sun Chung*

Received January 30, 1986

Complexes of the general formula $\text{CuL}(\text{SCN})_2$, where L = *N,N'*-bis(2-aminoethyl)-1,2-ethanediamine, *N,N'*-bis(2-aminoethyl)-1,3-propanediamine, *N,N'*-bis(3-aminopropyl)-1,3-propanediamine, *N,N'*-bis(3-aminopropyl)-1,2-ethanediamine, (1*SR*, 4*RS*, 7*RS*, 8*SR*, 11*SR*, 14*SR*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, (1*RS*, 4*RS*, 7*RS*, 8*SR*, 11*SR*, 14*SR*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, (1*SR*, 4*SR*, 7*SR*, 8*SR*, 11*SR*, 14*SR*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, (1*RS*, 4*SR*, 7*SR*, 8*RS*, 11*SR*, 14*SR*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, (1*RS*, 4*SR*, 8*RS*, 11*SR*, 14*SR*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, 1,4,8,11-tetraazacyclotetradecane, (1*SR*, 8*RS*)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, (1*SR*, 8*SR*)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, or 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene, have been prepared and characterized. Their infrared spectra were used to establish the bond type Cu-SCN or Cu-NCS. The dependence of the bond type on the structure of the coordinated quadridentate ligand in the complex is discussed.

Introduction

Metal-thiocyanato complexes have been extensively investigated in order to solve the interesting problem of whether the thiocyanato group is bonded to the metal through the nitrogen atom (M-NCS), through the sulfur atom (M-SCN), or through both by means of bridging (M-NCS-M).¹ It has been suggested by Pearson that S in SCN^- is soft and prefers to coordinate with soft acids (class b metals), whereas N in SCN^- is hard and coordinates with hard acids (class a metals).^{2,3} However, other factors such as the oxidation state of the metal, the nature of other ligands in the complex, and steric effects also influence the mode of coordination.⁴

In order to expand the knowledge in this area, we have initiated a systematic spectroscopic, thermodynamic, and kinetic study of inorganic linkage isomerism of this ambidentate ligand. This paper is concerned with the coordination of thiocyanate in some tetraamine and diimine-diamine complexes of copper(II). Copper(II) is on the borderline between hard and soft.⁵ The nature of the other ligands attached to it has a very great effect on the coordination behavior of the thiocyanate group. Ligand abbreviations used in this paper: 2,2,2-tet, *N,N'*-bis(2-aminoethyl)-1,2-ethanediamine; 2,3,2-tet, *N,N'*-bis(2-aminoethyl)-1,3-propanediamine; 3,3,3-tet, *N,N'*-bis(3-aminopropyl)-1,3-propanediamine; 3,2,3-tet, *N,N'*-bis(3-aminopropyl)-1,2-ethanediamine; tet a, *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetra-

(1) Mitchell, P. C. H.; Williams, R. J. P. *J. Chem. Soc.* **1960**, 1912-1918.
 (2) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533-3539.
 (3) Ahrland, S.; Chatt, J.; Davies, N. R. *Q. Rev. Chem. Soc.* **1958**, *12*, 265-276.

(4) Bennett, M. A.; Clark, R. J. H.; Goodwin, A. D. *J. Inorg. Chem.* **1967**, *6*, 1625-1631.
 (5) Yingst, A.; McDaniel, D. H. *Inorg. Chem.* **1967**, *6*, 1067-1068.

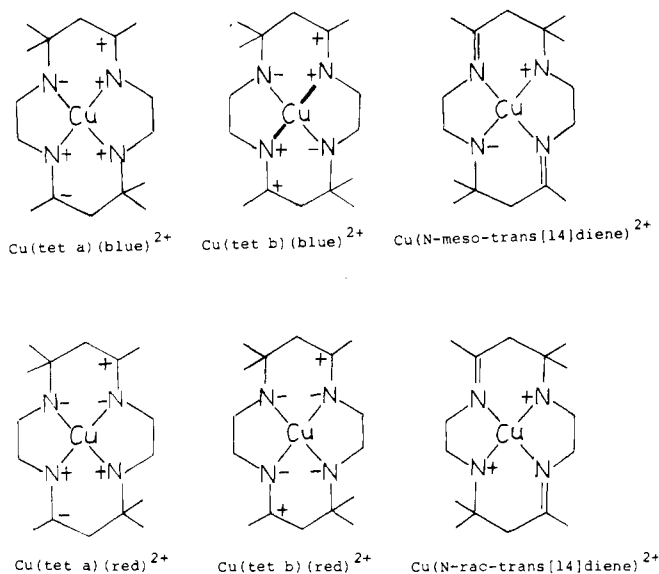


Figure 1. Configurations of $\text{Cu}(\text{tet a})(\text{blue})^{2+}$, $\text{Cu}(\text{tet a})(\text{red})^{2+}$, $\text{Cu}(\text{tet b})(\text{blue})^{2+}$, $\text{Cu}(\text{tet b})(\text{red})^{2+}$, $\text{Cu}(\text{N-meso-trans}[14]\text{diene})^{2+}$, and $\text{Cu}(\text{N-rac-trans}[14]\text{diene})^{2+}$. A plus sign at an asymmetric center indicates that the hydrogen atom of the center is above the plane of the macrocycle, and a minus sign, that it is below. For $\text{Cu}(\text{tet b})(\text{blue})^{2+}$, the heavier line indicates coordination with the macrocycle folded along this line.

decane; tet b, *C-rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; cyclam, 1,4,8,11-tetraazacyclotetradecane; Me_6cyclam , 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; trans[14]diene, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; cis[14]diene, 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene. Each of the following macrocyclic ligands, tet a, tet b, and trans[14]diene, forms two stereoisomers with copper(II), depending on the configurations of the coordinated secondary amines, which are asymmetric. The configurations of these isomers are represented in Figure 1.

Experimental Section

Reagents. All these ligands have been previously reported in the literature;⁶⁻¹⁵ their purity was established by microanalysis for carbon, hydrogen, and nitrogen.¹⁶ The complexes $\text{Cu}(\text{tet a})(\text{blue})(\text{ClO}_4)_2$, $\text{Cu}(\text{tet a})(\text{red})(\text{ClO}_4)_2$, $\text{Cu}(\text{tet b})(\text{blue})(\text{ClO}_4)_2$, $\text{Cu}(\text{tet b})(\text{red})(\text{ClO}_4)_2$, $\text{Cu}(\text{N-meso-trans}[14]\text{diene})(\text{ClO}_4)_2$, and $\text{Cu}(\text{N-rac-trans}[14]\text{diene})(\text{ClO}_4)_2$ used in this work were the same as those reported previously.^{6-8,17} The following complexes were prepared according to the methods described in the literature: $\text{Cu}(\text{cyclam})(\text{ClO}_4)_2$,¹⁰ $\text{Cu}(\text{Me}_6\text{cyclam})(\text{ClO}_4)_2$,¹¹ $\text{Cu}(3,2,3\text{-tet})(\text{ClO}_4)_2$,¹² $\text{Cu}(3,3,3\text{-tet})(\text{ClO}_4)_2$,¹² $\text{Cu}(\text{cis}[14]\text{diene})(\text{ClO}_4)_2$,¹³ $\text{Cu}(2,3,2\text{-tet})(\text{ClO}_4)_2$,¹⁴ and $\text{Cu}(2,2,2\text{-tet})(\text{ClO}_4)_2$.¹⁵

$[\text{Cu}(\text{tet b})(\text{red})(\text{SCN})](\text{NCS})$ and $[\text{Cu}(2,2,2\text{-tet})(\text{SCN})](\text{NCS})$ are already known.^{18,19} The other thiocyanate and isothiocyanate complexes were prepared by repeating the procedures for the preparation of CuL

Table I. Vibrational Frequencies (cm^{-1}) of the Thiocyanate Group in $\text{CuL}(\text{SCN})_2$ Complexes^a

complex	C-N str	C-S str	N-C-S bend
$[\text{Cu}(\text{tet a})(\text{blue})(\text{SCN})](\text{NCS})$	2082 sh 2058 s	728 m 750 m	429 m, 438 w 486 w, 470 m
$[\text{Cu}(\text{tet b})(\text{blue})(\text{NCS})](\text{SCN})$	2070 sp 2043 s	754 m 818 m	484 m, 470 m 472 m, 460 w
$[\text{Cu}(\text{tet a})(\text{red})(\text{NCS})_2]$	2067 s	825 w	482 m
$[\text{Cu}(\text{tet b})(\text{red})(\text{SCN})](\text{NCS})^{29}$	2092 s 2056 sp	708 m 744 m	430 m, 418 w 471 mw, 485 w
$[\text{Cu}(\text{Me}_6\text{cyclam})(\text{SCN})](\text{NCS})$	2082 s 2060 sh	729 m 750 m	429 m, 438 w 486 w, 471 m
$[\text{Cu}(\text{cyclam})(\text{NCS})_2]$	2060 s	810 m	485 m
$[\text{Cu}(\text{meso-trans}[14]\text{diene})(\text{NCS})_2]$	2060 s	812 m	488 mw
$[\text{Cu}(\text{rac-trans}[14]\text{diene})(\text{NCS})_2]$	2062 s	840 m	484 m
$[\text{Cu}(\text{cis}[14]\text{diene})(\text{NCS})_2]$	2070 s	816 m	486 mw
$[\text{Cu}(2,2,2\text{-tet})(\text{SCN})](\text{NCS})^{19}$	2080 s 2058 sh	718 m 748 w	423 mw, 433 w 485 m, 471 w
$[\text{Cu}(2,3,2\text{-tet})(\text{SCN})_2]$	2078 s	722 m	418 m, 430 w
$[\text{Cu}(3,3,3\text{-tet})(\text{SCN})_2]$	2082 s	721 m	425 mw, 434 w
$[\text{Cu}(3,2,3\text{-tet})(\text{SCN})](\text{NCS})$	2078 s 2056 sh	713 m 746 w	420 m, 431 w 485 mw, 470 m

^a Abbreviations: s, strong; m, medium; w, weak; sp, sharp; sh, shoulder.

Table II. Diffuse-Reflectance Spectra of Copper(II) Complexes

complex	λ_{max} , nm
$[\text{Cu}(\text{tet a})(\text{blue})(\text{SCN})](\text{NCS})$	668
$[\text{Cu}(\text{tet b})(\text{blue})(\text{NCS})](\text{SCN})$	858, 696
$[\text{Cu}(\text{tet a})(\text{red})(\text{NCS})_2]$	527
$[\text{Cu}(\text{tet b})(\text{red})(\text{SCN})](\text{NCS})$	540
$[\text{Cu}(\text{Me}_6\text{cyclam})(\text{SCN})](\text{NCS})$	670
$[\text{Cu}(\text{cyclam})(\text{NCS})_2]$	526
$[\text{Cu}(\text{meso-trans}[14]\text{diene})(\text{NCS})_2]$	522
$[\text{Cu}(\text{rac-trans}[14]\text{diene})(\text{NCS})_2]$	524
$[\text{Cu}(\text{cis}[14]\text{diene})(\text{NCS})_2]$	525
$[\text{Cu}(2,2,2\text{-tet})(\text{SCN})](\text{NCS})$	590
$[\text{Cu}(2,3,2\text{-tet})(\text{SCN})_2]$	543
$[\text{Cu}(3,3,3\text{-tet})(\text{SCN})_2]$	610
$[\text{Cu}(3,2,3\text{-tet})(\text{SCN})](\text{NCS})$	552

$(\text{ClO}_4)_2$,⁶⁻⁸ using NaSCN and HBF_4 in place of NaClO_4 and HClO_4 , respectively. These complexes were analyzed satisfactorily for carbon, hydrogen, nitrogen, and copper. These analytical data are available as supplementary material. All other chemicals used are commercially available.

Instrumentation. A Perkin-Elmer Model 580 spectrophotometer was used to measure infrared spectra. A Hitachi Model U-3200 spectrophotometer and a Cary 17 spectrophotometer with a thermostated cell compartment were used to measure electronic absorption spectra of the complexes.

Results and Discussion

The C-N stretching, C-S stretching, and NCS bending frequencies assigned to the copper(II) complexes are listed in Table I. It has previously been noted that a C-S stretching frequency of 780–860 cm^{-1} is indicative of N-bonding, while a frequency of 690–720 cm^{-1} indicates S-bonding.²⁰⁻²³ The C-N stretching frequencies are generally lower in the M-NCS complexes than in the M-SCN complexes.^{1,11} Furthermore, the NCS deformation mode can also be used to characterize the bond type, being a single band at 450–490 cm^{-1} for the M-NCS and a band at 400–440 cm^{-1} , with weaker satellites on the higher frequency side, for the M-SCN group.^{24,25} The assignments of the bands due to the thiocyanate groups were made by careful comparison of the spectra

- (6) Curtis, N. F. *J. Chem. Soc.* **1964**, 2644–2650.
- (7) Clay, R.; Murray-Rust, J.; Murray-Rust, P. *J. Chem. Soc., Dalton Trans.* **1979**, 1135–1139.
- (8) Margerum, D. W.; Bauer, R. A., unpublished work.
- (9) Curtis, N. F. *J. Chem. Soc.* **1960**, 4409–4412.
- (10) Barefield, E. K.; Wagner, F.; Hodges, K. D. *Inorg. Chem.* **1976**, *15*, 1370–1377.
- (11) Barefield, E. K.; Wagner, F. *Inorg. Chem.* **1973**, *12*, 2435–2439.
- (12) Hedwig, G. R.; Love, J. L.; Powell, H. K. *J. Aust. J. Chem.* **1970**, *23*, 981–987.
- (13) Love, J. L.; Powell, H. K. *J. Inorg. Nucl. Chem. Lett.* **1967**, *3*, 113–116.
- (14) Fawcett, T. G.; et al. *Inorg. Chem.* **1980**, *19*, 940–945.
- (15) House, D. A.; Curtis, N. F. *J. Chem. Soc.* **1963**, 3149–3151.
- (16) Wu, D.-T. Ph.D. Dissertation, National Tsing Hua University, Taiwan, Republic of China, 1986.
- (17) Palmer, J. M.; Papaconstantinou, E.; Endicott, J. F. *Inorg. Chem.* **1969**, *8*, 1516–1523.
- (18) Lu, T.-H.; Wu, D.-T.; Chung, C.-S. *J. Chem. Soc., Dalton Trans.*, in press.
- (19) Maronggi, G.; Lingafelter, E. C.; Paoletti, P. *Inorg. Chem.* **1969**, *8*, 2763–2767.

- (20) Nelson, S. M.; Shepherd, T. M. *J. Inorg. Nucl. Chem.* **1965**, *27*, 2123–2125.
- (21) Farago, M. E.; James, J. M. *Inorg. Chem.* **1965**, *4*, 1706–1711.
- (22) Lewis, J.; Nyholm, R. S.; Smith, P. W. *J. Chem. Soc.* **1961**, 4590–4599.
- (23) Sabatini, A.; Bertini, I. *Inorg. Chem.* **1965**, *4*, 959–961.
- (24) Sabatini, A.; Bertini, I. *Inorg. Chem.* **1965**, *4*, 1665–1667.
- (25) Bertini, I.; Sabatini, A. *Inorg. Chem.* **1966**, *5*, 1025–1028.

of the substituted thiocyanate complexes listed in Table I with those of the free amines and those of the corresponding halo complexes having the same configurations. The results given in Table I indicate that $[\text{Cu}(\text{tet b})(\text{blue})(\text{NCS})](\text{SCN})$, $[\text{Cu}(\text{tet a})(\text{red})(\text{NCS})_2]$, $[\text{Cu}(\text{cyclam})(\text{NCS})_2]$, $[\text{Cu}(\text{meso-trans}[14]\text{diene})(\text{NCS})_2]$, and $[\text{Cu}(\text{cis}[14]\text{diene})(\text{NCS})_2]$ are N-bonded, while $[\text{Cu}(\text{tet a})(\text{blue})(\text{SCN})](\text{NCS})$, $[\text{Cu}(\text{tet b})(\text{red})(\text{SCN})](\text{NCS})$, $[\text{Cu}(\text{Me}_4\text{cyclam})(\text{SCN})](\text{NCS})$, $[\text{Cu}(2,2,2\text{-tet})(\text{SCN})](\text{NCS})$, $[\text{Cu}(2,3,2\text{-tet})(\text{SCN})_2]$, $[\text{Cu}(3,3,3\text{-tet})(\text{SCN})_2]$, and $[\text{Cu}(3,2,3\text{-tet})(\text{SCN})](\text{NCS})$ are S-bonded.

$[\text{Cu}(\text{tet b})(\text{blue})(\text{NCS})](\text{SCN})$ is unique among these complexes. As shown in Table II, the electronic absorption spectrum of this complex in the solid state exhibits two d-d bands, while the spectra of the other copper(II) complexes in which the tetraamine or diimine-diamine ligand is in a planar or distorted-planar configuration exhibit a single λ_{max} . The crystal structures of $[\text{Cu}(\text{tet b})(\text{blue})(\text{H}_2\text{O})](\text{ClO}_4)_2$, $[\text{Cu}(\text{tet b})(\text{blue})]_2\text{Cl}(\text{ClO}_4)_3$, and $[\text{Cu}(\text{tet b})(\text{blue})(\text{NO}_3)](\text{ClO}_4)$ have been determined by three-dimensional X-ray methods.²⁶⁻²⁸ All these complexes contain trigonal-bipyramidal coordinated Cu^{2+} with the tet b ligand in its most stable, folded form. Four coordination positions of these complexes are rendered inert and stable by the strongly complexing tetraamine macrocyclic ligand, and the monodentate ligand, which occupies one of the positions in the trigonal plane, may exchange with other monodentate ligands.²⁹ The electronic spectrum of $[\text{Cu}(\text{tet b})(\text{blue})(\text{NCS})](\text{SCN})$ given in Table II is similar to that of $[\text{Cu}(\text{tet b})(\text{blue})(\text{H}_2\text{O})](\text{ClO}_4)_2$, $[\text{Cu}(\text{tet b})(\text{blue})]_2\text{Cl}(\text{ClO}_4)_3$, or $[\text{Cu}(\text{tet b})(\text{blue})(\text{NO}_3)](\text{ClO}_4)$. The two d-d bands indicate that $[\text{Cu}(\text{tet b})(\text{blue})(\text{NCS})](\text{SCN})$ contains trigonal-bipyramidal Cu^{2+} coordinated in a fashion similar to $[\text{Cu}(\text{tet b})(\text{blue})(\text{H}_2\text{O})](\text{ClO}_4)_2$, $[\text{Cu}(\text{tet b})(\text{blue})]_2\text{Cl}(\text{ClO}_4)_3$, and $[\text{Cu}(\text{tet b})(\text{blue})(\text{NO}_3)](\text{ClO}_4)$. The NCS^- , which occupies one of the positions in the trigonal plane, is N-bonded (Table I). There are two possible explanations for the mode of coordination: the nitrogen atom is a stronger σ donor than the sulfur atom; steric factors also favor the linear isothiocyanato group.

The crystal structures of $[\text{Cu}(\text{tet b})(\text{red})(\text{SCN})](\text{SCN})$ ¹⁸ and $[\text{Cu}(2,2,2\text{-tet})(\text{SCN})](\text{SCN})$ ¹⁹ have been determined by three-dimensional X-ray methods. The coordination around the central copper atom of each of these complexes is distorted square-pyramidal with the tetraamine ligand equatorial and the thiocyanato-S group axial. The axial Cu-S bond length is much longer than the Cu-N basal-plane bond length.^{18,19} Thus steric congestion may not have a great effect on the coordination behavior of the ambidentate ligand.

Although no structural information is available for the substituted thio- and isothiocyanato complexes of copper(II) reported here, the crystal structures of the corresponding halo or perchlorato complexes, $\text{Cu}(\text{tet a})(\text{red})(\text{ClO}_4)_2$,⁷ $\text{Cu}(\text{tet b})(\text{blue})(\text{ClO}_4)_2$,²⁶ $\text{Cu}(\text{Me}_4\text{cyclam})(\text{ClO}_4)_2$,³⁰ $\text{Cu}(\text{cyclam})(\text{ClO}_4)_2$,³¹ $\text{Cu}(N\text{-meso-trans}[14]\text{diene})(\text{ClO}_4)_2$,³² $\text{Cu}(N\text{-rac-trans}[14]\text{diene})(\text{ClO}_4)_2$,³³ $\text{Cu}(3,3,3\text{-tet})(\text{ClO}_4)_2$,¹⁴ $\text{Cu}(2,3,2\text{-tet})(\text{ClO}_4)_2$,¹⁴ and $\text{Cu}(3,2,3\text{-tet})(\text{ClO}_4)_2$,³⁴ have been determined. For each of these complexes, the coordination around the copper atom is a square pyramid, a distorted square pyramid, or a tetragonally distorted octahedron with the tetraamine or the diimine-diamine ligand equatorial and the monodentate ligand or ligands axial. The electronic and infrared spectral data suggest the thiocyanato or isothiocyanato

Table III. Electronic Absorption Spectra of Copper(II) Complexes in Aqueous Solution at 25.0 °C and $\mu = 0.1 \text{ M} (\text{NaClO}_4)$

complex	λ_{max} , nm	ϵ_{max} , $\text{M}^{-1} \text{ cm}^{-1}$
$[\text{Cu}(\text{tet a})(\text{blue})](\text{ClO}_4)_2$	650	210
$[\text{Cu}(\text{tet b})(\text{blue})](\text{ClO}_4)_2$	834, 680 sh	269, 172
$[\text{Cu}(\text{tet a})(\text{red})](\text{ClO}_4)_2$	512	135
$[\text{Cu}(\text{tet b})(\text{red})](\text{ClO}_4)_2$	525	174
$[\text{Cu}(\text{Me}_4\text{cyclam})](\text{ClO}_4)_2$	650	260
$[\text{Cu}(\text{cyclam})](\text{ClO}_4)_2$	510	85
$[\text{Cu}(\text{meso-trans}[14]\text{diene})](\text{ClO}_4)_2$	501	122
$[\text{Cu}(\text{rac-trans}[14]\text{diene})](\text{ClO}_4)_2$	504	105
$[\text{Cu}(\text{cis}[14]\text{diene})](\text{ClO}_4)_2$	506	128
$[\text{Cu}(2,2,2\text{-tet})](\text{ClO}_4)_2$	580	150
$[\text{Cu}(2,3,2\text{-tet})](\text{ClO}_4)_2$	527	70
$[\text{Cu}(3,3,3\text{-tet})](\text{ClO}_4)_2$	597	173
$[\text{Cu}(3,2,3\text{-tet})](\text{ClO}_4)_2$	543	92

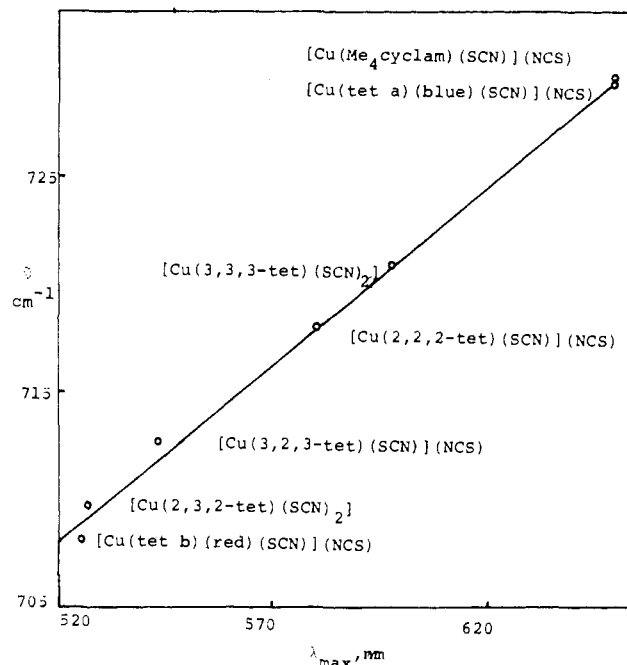


Figure 2. Plot of the C-S stretching frequency of $\text{CuL}(\text{SCN})_2$ against the electronic absorption maximum for $\text{CuL}(\text{ClO}_4)_2$.

complexes have the same configurations as their corresponding halo or perchlorato complexes; i.e., the four nitrogen atoms of the quadridentate ligand are in the strongly coordinating equatorial positions and the monodentate ligand occupies the elongated axial position. The axial bond is long, and therefore steric effects should not affect the coordination behavior of the ambidentate ligand.^{18,19}

It is interesting to note that the axial thiocyanate group is bonded to $\text{Cu}(\text{II})$ through the nitrogen atom or through the sulfur atom, depending on the nature of the coordinated tetradentate ligand in the complex. Although the sulfur atom is a weaker σ donor than the nitrogen atom,³⁵ M-S bonding is stabilized by π back-bonding from metal to sulfur and when there is a great degree of back-bonding of metal nonbonding electrons into vacant antibonding π -orbitals of the thiocyanate group, the M-S π bond is so increased in strength that the S-bonded isomer becomes the more stable one. For complexes in which the four donor nitrogen atoms of the tetraamine ligand form a perfect plane, the energy levels of the metal nonbonding d_{xz} and d_{yz} orbitals are relatively low, and the degree of back-bonding of the metal nonbonding electrons of these orbitals into vacant antibonding π -orbitals of the axial thiocyanate group is small, resulting in the formation of the N-bonded isomer. As the distortion of the plane of the four amino nitrogen atoms increases, the degree of back-coordination increases, and the S-bonded isomer becomes the more stable one. The wavelength of the maximum of the d-d band of $\text{CuL}(\text{ClO}_4)_2$,

(26) Sheu, H.-R.; Lee, T.-J.; Chung, C.-S. *Proc. Natl. Sci. Council, Repub. China, Part B* **1983**, *7*, 113-118.

(27) Bauer, R. A.; Robinson, W. R.; Margerum, D. W. *J. Chem. Soc., Chem. Commun.* **1973**, 289-290.

(28) Lee, T.-J.; Lee, Y.-J.; Lee, C.-S.; Chung, C.-S. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 641-644.

(29) Lee, C.-S.; Chung, C.-S. *Inorg. Chem.* **1984**, *23*, 4162-4166.

(30) Lee, T.-J.; Wu, D.-T.; Chung, C.-S., submitted for publication in *Acta Crystallogr.*

(31) Tasker, P. A.; Sklar, L. J. *Cryst. Mol. Struct.* **1975**, *5*, 329-344.

(32) Lee, T.-J.; Lu, T.-H.; Chung, C.-S.; Lee, T.-Y. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 70-72.

(33) Lu, T.-H.; Lee, T.-J.; Liang, B.-F.; Chung, C.-S. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2333-2336.

(34) Lee, T. J.; Wu, D.-T.; Chung, C.-S., submitted for publication in *Acta Crystallogr.*

(35) Burmeister, J. L.; Basolo, F. *Inorg. Chem.* **1964**, *3*, 1587-1593.

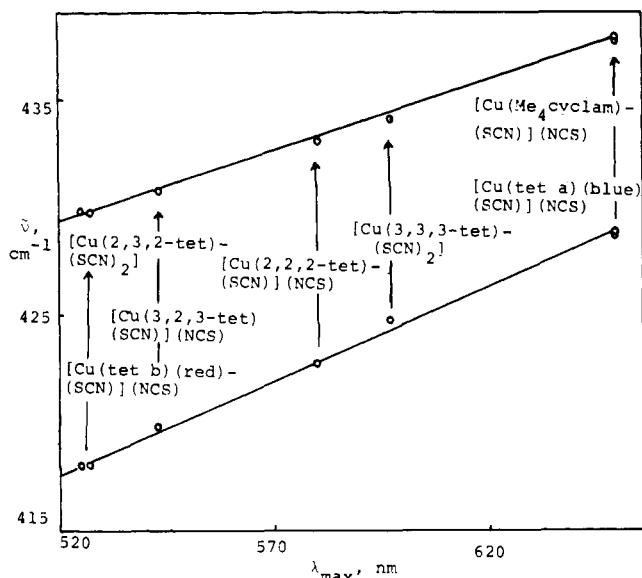
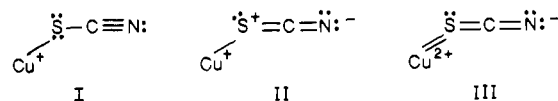


Figure 3. Plot of the N-C-S bending frequencies of $\text{CuL}(\text{SCN})_2$ against the electronic absorption maximum for $\text{CuL}(\text{ClO}_4)_2$.

where L is a tetraamine or a diimine-diamine ligand, in aqueous solution (Table III) is considered an approximate measure of the degree of distortion of the CuN_4 plane.^{36,37} As shown in Table III, when the absorption maximum for $\text{CuL}(\text{ClO}_4)_2$ is larger than 525 nm, the degree of distortion of the CuN_4 plane is large and the thiocyanato group is bonded to Cu(II) through the sulfur atom (M-SCN); when the absorption maximum for $\text{CuL}(\text{ClO}_4)_2$ is smaller than 525 nm, the degree of distortion of the CuN_4 plane is small and the axial isothiocyanato group is bonded to Cu(II) through the nitrogen atom (M-NCS).

For these S-bonded copper(II) complexes, it is interesting to note that both the C-S stretching frequency and the N-C-S bending frequencies of the axial thiocyanato-S group increase as the wavelength of the maximum of the d-d band of the complex

increases, i.e. $[\text{Cu}(\text{tet b})(\text{red})(\text{SCN})](\text{NCS}) < [\text{Cu}(2,3,2\text{-tet})(\text{SCN})_2] < [\text{Cu}(3,2,3\text{-tet})(\text{SCN})](\text{NCS}) < [\text{Cu}(2,2,2\text{-tet})(\text{SCN})](\text{NCS}) < [\text{Cu}(3,3,3\text{-tet})(\text{SCN})_2] < [\text{Cu}(\text{Me}_4\text{cyclam})(\text{SCN})](\text{NCS})$, $[\text{Cu}(\text{tet a})(\text{blue})(\text{SCN})](\text{NCS})$. In general, three resonance structures (I-III) can be written for the thiocyanato-S group, with I somewhat more important than each of the other two.



As the degree of back-bonding of metal nonbonding electrons into vacant antibonding π -orbitals of the thiocyanato-S group increases, the contribution of structure III increases; the C-S bond order thus increases, as do the C-S stretching frequency and N-C-S bending frequencies. For the same reasons discussed previously the degree of back-bonding increases as the distortion of the plane of the four amino nitrogen atoms increases. These trends lead us to think that there may be a linear relationship between the C-S stretching frequency of $\text{CuL}(\text{SCN})_2$ and the electronic absorption maxima for $\text{CuL}(\text{ClO}_4)_2$ and a linear relationship between the N-C-S bending frequencies of $\text{CuL}(\text{SCN})_2$ and the electronic absorption maxima for $\text{CuL}(\text{ClO}_4)_2$. These suggested linear relationships are shown in Figures 2 and 3.

Acknowledgment. The support of the Chemistry Research Center, National Science Council of the Republic of China, under Grants NSC 74-0208-M007-08 and NSC 75-0208-M007-04 is gratefully acknowledged. We are grateful to Dr. Chi-Chao Wan and Yuan-Chung Hsieh for performing elemental analyses and for providing laboratory facilities.

Registry No. $[\text{Cu}(\text{tet b})(\text{blue})(\text{NCS})](\text{SCN})$, 103530-17-2; $[\text{Cu}(\text{cyclam})](\text{NCS})_2$, 103439-52-7; $[\text{Cu}(\text{Me}_4\text{cyclam})(\text{SCN})](\text{NCS})$, 103439-54-9; $[\text{Cu}(N\text{-meso-trans}[14]\text{diene})](\text{NCS})_2$, 103439-55-0; $[\text{Cu}(N\text{-rac-trans}[14]\text{diene})](\text{NCS})_2$, 103439-56-1; $[\text{Cu}(\text{cis}[14]\text{diene})](\text{NCS})_2$, 103439-57-2; $[\text{Cu}(\text{tet a})(\text{blue})(\text{SCN})](\text{NCS})$, 103530-18-3; $[\text{Cu}(\text{tet a})(\text{red})(\text{NCS})_2]$, 103439-58-3; $[\text{Cu}(\text{tet b})(\text{red})(\text{SCN})](\text{NCS})$, 103530-20-7; $[\text{Cu}(2,2,2\text{-tet})(\text{SCN})](\text{NCS})$, 24555-89-3; $[\text{Cu}(2,3,2\text{-tet})(\text{SCN})_2]$, 103439-59-4; $[\text{Cu}(3,3,3\text{-tet})(\text{SCN})_2]$, 103439-60-7; $[\text{Cu}(3,2,3\text{-tet})(\text{SCN})](\text{NCS})$, 103439-62-9.

Supplementary Material Available: A table showing the analytical data of the thiocyanate and isothiocyanate complexes (1 page). Ordering information is given on any current masthead page.

(36) Liang, B.-F.; Chung, C.-S. *Inorg. Chem.* 1980, 19, 572-574.

(37) Wu, S.-Y.; Lee, C.-S.; Chung, C.-S. *Inorg. Chem.* 1984, 23, 2548-2550.

Contribution from the Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

Room-Temperature Fused Salts Based on Copper(I) Chloride-1-Methyl-3-ethylimidazolium Chloride Mixtures. 2. Reactions with Dioxigen¹

Steven A. Bolkan and John T. Yoke*

Received March 11, 1986

As the composition of $n/(1-n)$ $\text{CuCl}/\text{MeEtImCl}$ melts is varied, the apparent stoichiometry of the reaction with O_2 in the course of several days at 33 °C varies from about 8/1 $\text{Cu(I)}/\text{O}_2$ at $n = 0.60$ to 4/1 $\text{Cu(I)}/\text{O}_2$ at $n = 0.50$. At a higher temperature, or at $n = 0.40$ at 33 °C, more O_2 is taken up, and in addition to oxidation of copper, formation of 1-methyl-3-ethylimidazolone and water is extensive. The viscous black liquid products show anomalous paramagnetism and catalyze the oxidative polymerization or coupling of 2,6-dimethylphenol. When heated in vacuo, they lose water and the residue is nearly diamagnetic. The organic salt MeEtImCl does not react with O_2 . When CuCl_2 and CuO are heated with MeEtImCl to 100 °C in vacuo, a black liquid is formed containing 1-methyl-3-ethylimidazolone.

Introduction

Physical properties have been reported² for mixtures of copper(I) chloride and 1-methyl-3-ethylimidazolium chloride, $n/(1-n)$ $\text{CuCl}/\text{MeEtImCl}$. These mixtures are liquid electrolytes

down to about -50 °C over the mole fraction range $0.33 \leq n \leq 0.67$. They may have practical application in batteries. Their electrochemical properties will be described separately.³ The melts, whose colors vary from pale yellow to light green with increasing n , darken rapidly in air and become paramagnetic as copper(II) is formed.

(1) Taken from the Ph.D. Dissertation of S.A.B.; supported in part by a grant from the Oregon State University Research Council.

(2) Bolkan, S. A.; Yoke, J. T. *J. Chem. Eng. Data*, 1986, 31, 194.

(3) Bolkan, S. A.; Yoke, J. T., to be submitted for publication.