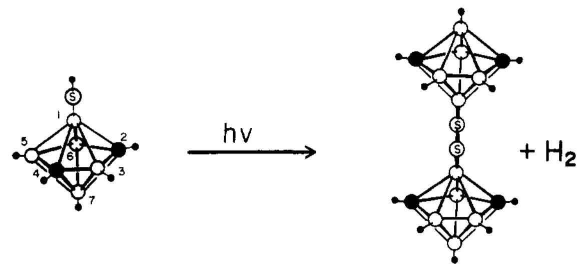


Figure 2. Synthesis of 1,1′-$(2,4\text{-}C_2B_5H_6)_2$ from 1-SH-2,4-$C_2B_5H_6$.

As mentioned above, the studies[4] of the reactions of atomic sulfur with alkanes demonstrated that only ^1D sulfur atoms gave C–H insertion products, while $^3P_1$ sulfur atoms did not react with alkanes. Our studies are analogous to the studies on alkanes, since mercury sensitizing the reactions suppresses the formation of mercaptocarborane products.

The reaction of ^1D sulfur atoms with 2,4-$C_2B_5H_7$ also gave several compounds which are the first examples of boron bonded bridging disulfide groups: 1,1′-S_2-(2,4-$C_2B_5H_6$), 5,5′-S_2-$(2,4\text{-}C_2B_5H_6)_2$, and 3,3′-S_2-(2,4-$C_2B_5H_6$). Although we have isolated only three such compounds, we have evidence that all possible linked combinations exist, but the small amounts produced, or difficult separations, precluded complete characterization of all such compounds. The formation of the disulfides in the original reaction suggested that the mercaptans formed may have been undergoing some secondary photolytic decomposition, followed by recombination of the resulting radicals:

$$C_2B_5H_6SH \xrightarrow{h\nu} C_2B_5H_6S\cdot + H\cdot$$

$$2\,H\cdot \rightarrow H_2$$

$$2C_2B_5H_6S\cdot \rightarrow S_2\text{-}(C_2B_5H_6)_2$$

To test this possibility separate pure samples of 1-SH-2,4-$C_2B_5H_6$ and 3-SH-2,4-$C_2B_5H_6$ were photolyzed and were found to convert to the corresponding disulfides 1,1′-S_2-$(2,4\text{-}C_2B_5H_6)_2$ and 3,3′-S_2-$(2,4\text{-}C_2B_5H_6)_2$ in good yields (Figure 2).

The disulfides are especially interesting since they appear to be both hydrolytically and thermally stable. Also, like the mercaptans, the disulfides are boron-substituted, therefore leaving the cage carbon positions open for substitution or polymerization reactions. We hope to explore the chemistry of these compounds, as well as their possible applications, in the future.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant DMR 72-03025) for the partial support of this research.

References and Notes

(1) P. L. Timms, *Adv. Inorg. Chem. Radiochem.*, **14**, 121 (1972).
(2) For examples, see *Angew. Chem., Int. Ed. Engl.*, **14**, 193–222 and 273–303 (1975).
(3) H. E. Gunning and O. P. Strausz, *Adv. Photochem.*, **4**, 143 (1966).
(4) (a) A. R. Knight, O. P. Strausz, and H. E. Gunning, *J. Am. Chem. Soc.*, **85**, 1207 (1963); (b) *ibid.*, **85**, 2349 (1963); (c) A. R. Knight, O. P. Strausz, S. M. Malm, and H. E. Gunning, *ibid.*, **86**, 4243 (1964).
(5) I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, *J. Am. Chem. Soc.*, **85**, 3167 (1963).
(6) R. N. Grimes, *J. Am. Chem. Soc.*, **88**, 1895 (1966).
(7) N. J. Maraschin and R. J. Lagow, *Inorg. Chem.*, **14**, 1855 (1975).
(8) R. Warren, D. Paquin, T. Onak, G. Dunks, and J. R. Spielman, *Inorg. Chem.*, **9**, 2285 (1970).
(9) J. F. Ditter, E. B. Klusmann, R. E. Williams, and T. Onak, *Inorg. Chem.*, **15**, 1063 (1976).
(10) D. Marynick and T. Onak, *J. Chem. Soc. A*, 1797 (1969).
(11) (a) H. D. Smith, C. O. Obenland, and S. Papetti, *Inorg. Chem.*, **5**, 1013 (1966); (b) N. S. Semenuk, S. Papetti, and H. Schroeder, *ibid.*, **8**, 2441 (1969).
(12) L. I. Zakharkin and G. G. Zhigareva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1358 (1967).
(13) Although cage insertion of sulfur atoms to give *nido*-dicarbathioboranes was also considered a possibility, no evidence for the formation of the compounds was obtained.
(14) W. L. Jolly, "The Principles of Inorganic Chemistry", McGraw-Hill, New York, N.Y., 1976, p 41.
(15) L. I. Zakharkin and V. N. Kalinin, *Dokl. Akad. Nauk SSSR*, 1091 (1967).

Electronic Structure of Macrocyclic Compounds Revealed by X-Ray Photoelectron Spectroscopy

Manabu Senō,* Shinji Tsuchiya, and Shojiro Ogawa

Contribution from the Institute of Industrial Science, The University of Tokyo, 7-22, Roppongi, Minato-Ku, Tokyo 106, Japan. Received August 26, 1976

Abstract: The electronic and stereochemical structures of tetraaza macrocycle, hexaaza macrocycle, and their metal complexes have been clarified by x-ray photoelectron spectroscopy and magnetic susceptibility measurements. These macrocycles have the delocalized structure of inner hydrogens, whereas tetraphenylporphine has the bonded structure. Most of the metal complexes, except for the cobalt complex, have square planar structure. The structure of the cobalt complex over the temperature range 140–210 K is supposed to be square planar, but there was observed a transition temperature at about 210 K.

A high level of interest has been directed recently to the chemistry of porphyrins and metalloporphyrins owing to their biological importance, and the properties and the structure of these compounds have been studied by many physical methods.[1] For example, the extensive x-ray data on single crystals indicated that the atoms of the inner ring are individually planar and the bond distances of this ring resemble those of a heterocyclic aromatic system.[2] The measurements of x-ray photoelectron spectroscopy (XPS) showed a bonded structure of the inner hydrogens and elucidated the difference in the electron densities between the aza nitrogen and the pyrrole nitrogen in the metal-free tetraphenylporphine.[3]

Some synthetic tetraaza macrocycles have been also studied as porphyrin models.[4] An elucidation of the electronic and stereochemical properties of these macrocycles may give some useful information regarding the behavior of metalloporphyrins

Table I. N 1s Binding Energies and fwhm[a] of the Macrocycles, Their Metal Complexes, and Related Compounds

	N 1s, eV	fwhm[a]
(1) Tetraaza macrocycle	397.5	1.5
(2) Hexaaza macrocycle	399.2, 397.7	1.5
(3) [Hexaaza macrocycle]2HCl	398.6	3.3
(4) Ni complex[hexaaza macrocycle]	398.0	2.4
(5) Co complex[hexaaza macrocycle]	398.0	2.3
(6) Cu complex[hexaaza macrocycle]	397.6	2.0
(7) 2,9-Diamino-1,10-phenanthroline	398.1	1.7
(8) 2,9-Dichloro-1,10-phenanthroline	398.2	1.5
(9) $(CH_3)_2\underset{CH_2C_6H_4NO_2}{\underset{\vert}{N^+}}N^-COCH_3$	405.1, 401.4, 397.5[b]	1.5
(10) $[(CH_3)_2\underset{CH_2C_6H_4NO_2}{\underset{\vert}{N^+}}NHCOCH_3]Br^-$	405.0, 402.5, 400.1[b]	1.5

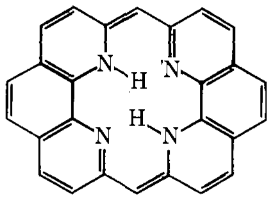
[a] The full widths at half-maximum. [b] Reference 9.

in the living systems, and particularly the interaction between the gases and the macrocycles. Baldwin et al. reported that the reversibility of adsorption of oxygen molecules on iron(II) macrocycles is dependent upon the steric hindrance provided by the ligands,[5] and Traylor et al. reported a large effect of the structure of the proximal nitrogen base upon the differential affinity of heme complexes for oxygen and carbon monoxide.[6] Collman et al. demonstrated several cycles of reversible oxygenation at room temperature with "picket fence" porphyrins, having steric shielding on one side of the porphyrin.[7]

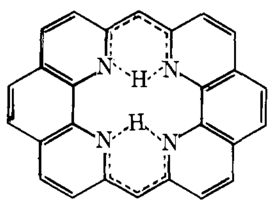
We now report the electronic and stereochemical structures of novel macrocycles and their metal complexes, the synthesis of which we recently described,[8] by means of XPS and magnetic susceptibilities.

Results and Discussion

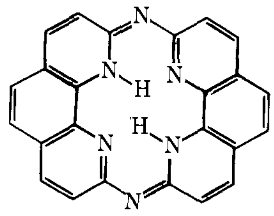
XPS Studies. We have been interested in the macrocycles useful for the synthetic porphyrin models, and found that the macrocycles **1** and **2** contained the conjugated forms similar to porphyrins. Two possible structures arising from the location of hydrogens in conjugated forms of tetraaza macrocycles **1a** and **1b** or hexaaza macrocycles **2a** and **2b** are shown as follows.



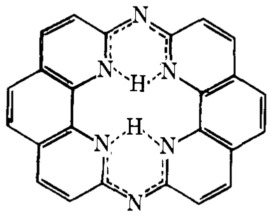
1a



1b



2a



2b

The observed N 1s binding energies are summarized in Table I, which contains all the values of binding energy of macrocycles, their metal complexes, and the related compounds.

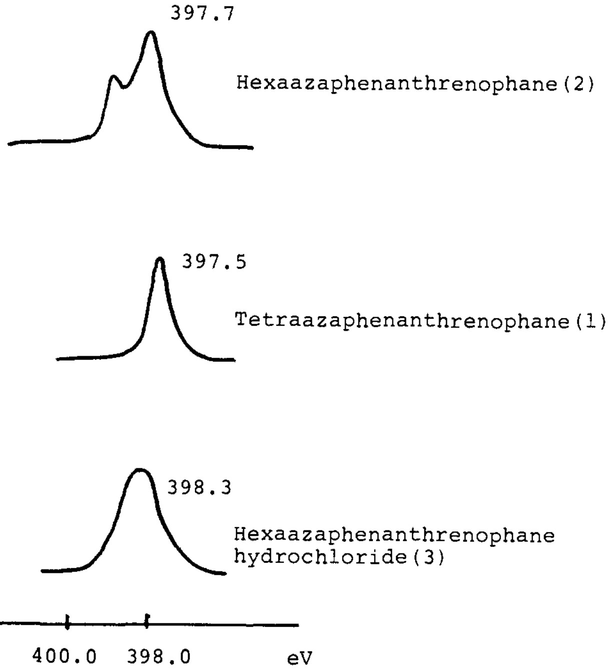


Figure 1. N 1s spectra of macrocycles.

Zeller and Niwa observed two peaks in N 1s spectra of tetraphenylporphine, and Niwa et al. concluded that each of the central two hydrogens in the metal-free bases is localized on one of the central four porphinato nitrogens.[3] On the other hand, the N 1s spectrum of macrocycle **1** used in this study gave only a single peak, and the full width at half-maximum (fwhm) is 1.5 eV as shown in Figure 1. In the N 1s spectrum of **2**, two separate peaks were observed, and the energy difference (ΔE) between two peaks was 1.5 eV and the observed relative intensity was 1:2. The binding energy for the larger peak in the spectrum of macrocycle **2** is close to the energy of nitrogens in macrocycle **1**. We already reported the XPS of aminimides, and the N 1s spectrum shows a large chemical shift of the peaks arising from a ylidic nitrogen, a quaternary nitrogen, and a nitro nitrogen as shown in Figure 2.[9] Then we used the aminimide **9** as an internal reference check for the XPS measurement of the macrocycles. Mixed grinding of macrocycle **2** with the aminimide **9** appeared to be useful for the estimation of the electron density on the nitrogens of macrocycle **2**. The procedure involved recording the N 1s binding energy of macrocycle **2** and then diluting the macrocycle **2** with an excess amount of aminimide **9**. The N 1s spectra of the reference aminimide **9** and the mixture of macrocycle **2** and aminimide **9** are shown in Figure 2. The spectrum of the corresponding salt of aminimide **9** is shown in the same figure. The sharp peaks with fwhm of 1.5 eV of the highest and the second

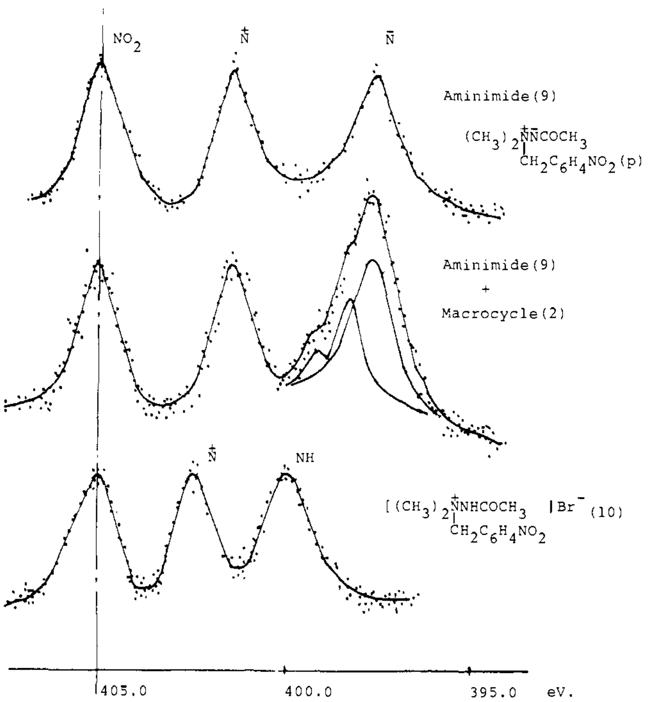
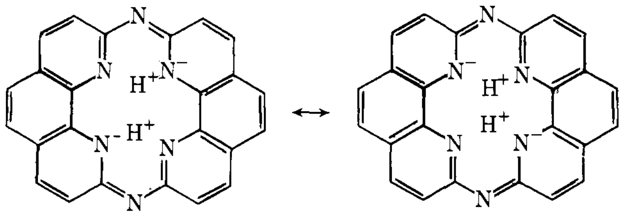


Figure 2. N 1s spectra of aminimide **9**, salt **10**, and macrocycle **2**.

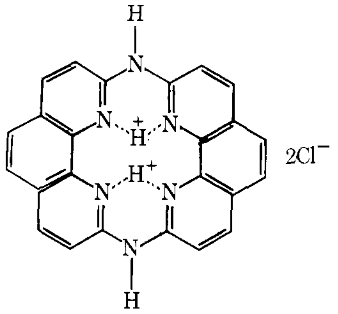
binding energy of the mixture arise from the nitro nitrogen and the quaternary nitrogen of the aminimide, respectively. However, the lowest binding energy peak is an unsymmetrical broad one having two shoulders. The position of the main peak of lowest binding energy peak is consistent with that of ylidic nitrogen (N^-) of aminimide **9**, and therefore the two shoulders are assigned to the peaks of macrocycle **2**.

The three peaks assigned to aminimide **9** in the spectrum of the mixture are coincident with the original spectrum of aminimide **9**. This indicates that the interaction between aminimide **9** and macrocycle **2** scarcely exists. Then if we assign zero charge to the nitrogen (NH) of the salt, the central nitrogens of macrocycle **2** should have some negative charge which is less than that of the ylidic nitrogen (N^-) of aminimide **9**. These results suggest that macrocycle **2** has the delocalized structure having ionic character; that is, two cationic hydrogens, four electron-rich nitrogens (central), and two neutral nitrogens (bridging) as shown in the following scheme.



This conclusion is supported by measurements of IR and ^{1}H NMR. The ν(N-H) band of macrocycle **2** appears at 2780 cm^{-1}, and this value is much lower than that of porphine (3324 cm^{-1}), which has a localized structure. The ^{1}H NMR measurements also convince us of the cationic character of inner hydrogens; that is, the peak of the inner hydrogens for macrocycle **2** appears at extremely low magnetic field (δ 18.5 ppm in TFA).

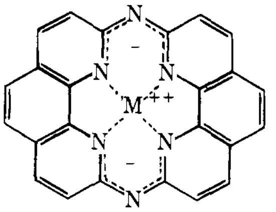
The N 1s spectrum of hexaaza macrocycle hydrochloride **3** shows a single peak with large fwhm of 3.3 eV, and the binding energy is higher than that of the main peak of the corresponding macrocycle **2**. These facts suggest that the electronic charge of six nitrogen atoms is equalized by hydrochlorination, and macrocycle hydrochloride **3** is assumed to have the electronic structure shown below.



3

This structure also contains the hydrogens of cationic character similar to the structure supposed for macrocycle **2**.

All the peaks of metal complexes of macrocycle **2** do not show any splitting; the fwhm of these peaks (2.0–2.4 eV) is considerably large and the N 1s binding energies of these complexes are higher than that of the main peak of original macrocycle **2**. These indicate that π electron in metal complexes is delocalized through metal ion and nitrogen atoms of the macrocycle as shown below.



The Ni 2p, Co 2p, and Cu 2p binding energies of the metal complexes are summarized in Table II, and their spectra are shown in Figure 3. Frost et al. reported that the cupric compounds have satellites, while the cuprous compounds have no satellites associated with each main peaks, and the width of the main peaks of the cuprous compounds is narrower than that of the cupric.[10] As shown in Figure 3, the Cu 2p line of cupric chloride from which hexaaza macrocycle–copper complex **6** is prepared has large satellites, while the Cu 2p line of macrocycle–copper complex **6** has narrow parent lines and small satellites. It could be pointed out from this result that the copper of macrocycle complex **6** has a monovalent character owing to the coordination of electron-rich nitrogen. Hence, it is expected that these complexes have the ability of reduction similar to the porphyrin–metal complexes.

We discussed the correlation between stereochemical structure and satellites of nickel compounds in a preceding paper;[11] the 2p binding energies of the nickel ion increase in the order planar < tetrahedral < octahedral, and for paramagnetic nickel compounds, the parent lines are broad, being accompanied by large satellites, whereas for diamagnetic nickel compounds, the narrow parent lines with no or very small satellites are observed. As shown in Figure 3, no satellites are observed on the core level of nickel and the Ni 2p binding energies are low and close to those of square-planar complexes reported previously[11] for macrocycle–nickel complex **4**. This suggests that hexaaza macrocycle nickel complex **4** is of a square-planar structure, though a wide variety of nonplanar porphyrins (pyramidal or octahedral) has been often found.

Magnetic Susceptibilities Studies. We are also interested in the magnetic properties of these macrocycle–metal complexes. Hexaaza macrocycle–nickel complex **4** is diamagnetic, while hexaaza macrocycle–cobalt complex **5** and hexaaza macrocycle–copper complex **6** are paramagnetic. Then, in order to

Table II. Ni 2p, Co 2p, and Cu 2p Binding Energies of Macrocycle Complexes and Related Compounds (eV)

	Ni $2p_{3/2}$	Sat.	Ni $2p_{1/2}$	Sat.[a]
(4)Ni-hexaaza macrocycle complex	854.3		872.3	
Ni-phthalocyanine complex	854.6		872.3	
$NiCl_2$	857.3	862.6	874.5	878.8[b]
$Ni[P(n\text{-}C_4H_9)_3]_2Cl_2$	854.3	861.8	871.7	[b]
	Co $2p_{3/2}$	Co $2p_{1/2}$		
(5)Co-hexaaza macrocycle complex	779.7	795.5		
Co-tetraphenylporphine complex	778.8[c]			
	Cu $2p_{3/2}$	Sat.	Cu $2p_{1/2}$	Sat.
(6)Cu-hexaaza macrocycle complex	934.1	943.4	954.2	963.2
$CuCl_2$	934.1	941.4 943.9	953.9	962.7

[a] Satellite. [b] M. Senō, S. Tsuchiya, M. Hidai, and Y. Uchida, *Bull. Chem. Soc. Jpn.*, **49**, 1184 (1976). [c] M. V. Zeller and R. G. Hayes, *J. Am. Chem. Soc.*, **95**, 3855 (1973).

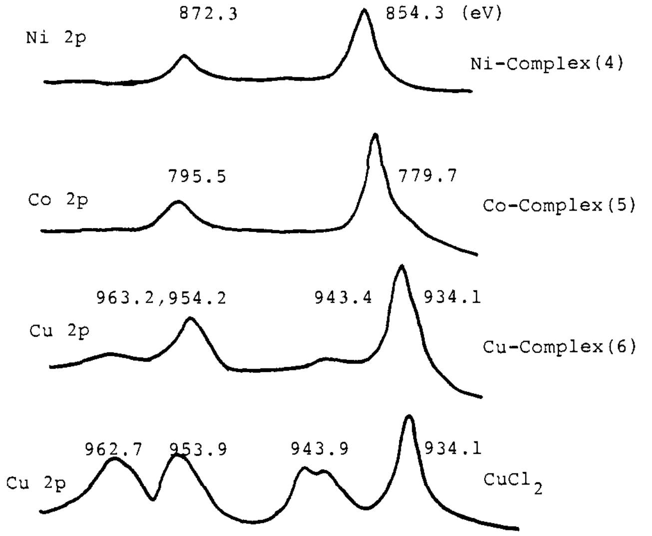


Figure 3. Ni 2p, Co 2p, and Cu 2p spectra of hexaaza macrocycle metal complexes and related compounds.

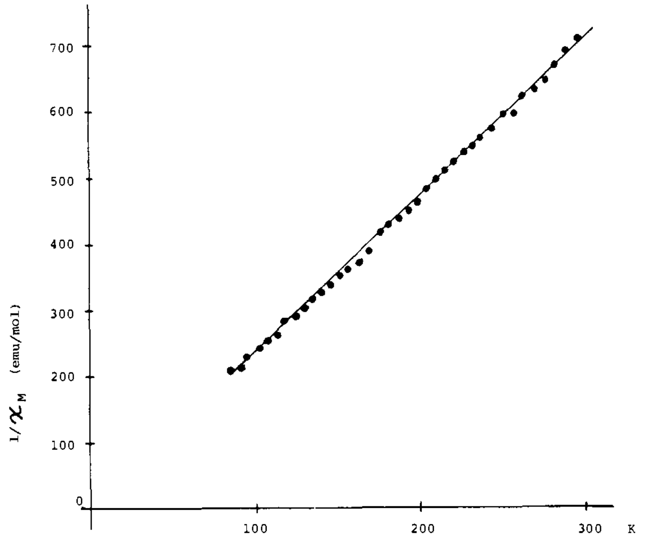


Figure 4. Magnetic susceptibility of copper hexaaza macrocycle complex (**6**).

get further information, the susceptibilities of copper complex **6** and cobalt complex **5** were measured over a range of temperature and discussed in detail on the stereochemistry of these complexes.

Many measurements have been carried out on magnetic properties of bivalent copper compounds and these studies have established the correlation between the magnetic moment and the stereochemistry or the bond type. Ray and Sen correlated the magnetic moments of 1.7–1.9 μ_B with a red-yellow color, and of 1.9–2.2 μ_B with a green-blue color of copper complexes,[12] and attributed the latter group to a tetrahedral stereochemistry of the ligands and the former group to an octahedral arrangement. In addition, Figgis et al. reported that, for the square-planar complexes $Cu(acetylacetone)_2$, $Cu(dimethylglyoxime)Cl_2$, and $Cu(o\text{-phenanthroline})_2(ClO_4)_2$, the magnetic moments were found to be about 1.90 μ_B (1.90, 1.85, and 1.89 μ_B, respectively).[13] As shown in Figure 4, the change of the magnetic property of the red-brown copper complex **6** with temperature is monotonous. The moment of this complex is found to be about 1.85 μ_B, and this value is close to those of square-planar complexes as described above. Hence, in spite of the absence of x-ray analyses, it is reasonable for complex **6** to assign the square-planar structure of the ligands around the cupric ion.

Figgis described also the relation between the magnetic moments and the stereochemistry of cobalt compounds and concluded from a survey of data available in the literature that for spin-paired square complexes the moments range from 2.1 to 2.9 μ_B including a very high orbital contribution, while for spin-paired octahedral complexes, the orbital contribution is generally low, and the moments fall in the range of 1.7–2.0 μ_B.[14] The result of measurements on the magnetic properties of cobalt complex **5** over the temperature range of 140–296 K is set out in Figure 5. The striking feature of this result is that the magnetic behavior of this complex **5** is not simple; the line has a break at about 210 K, where the magnetic moment changes abruptly. In the temperature range of 140–210 K, the moment is 2.47 μ_B and this value lies within the range reported for the spin-paired square planar complexes. The excess over the "spin only" value of 1.73 μ_B would be attributable to incomplete quenching of the orbital contribution, and it seems plausible to conclude that cobalt complex **5** has a square-planar structure in the temperature range of 140–210 K. On the other hand, in the temperature range of 210–296 K, the moment is 1.75 μ_B; this value is close to the "spin only" value (1.73 μ_B) of the spin-pair type. Although these moments were obtained from the slopes of the temperature dependence curve, the magnetic susceptibility of complex **5** is 2.24×10^{-3} emu/mol

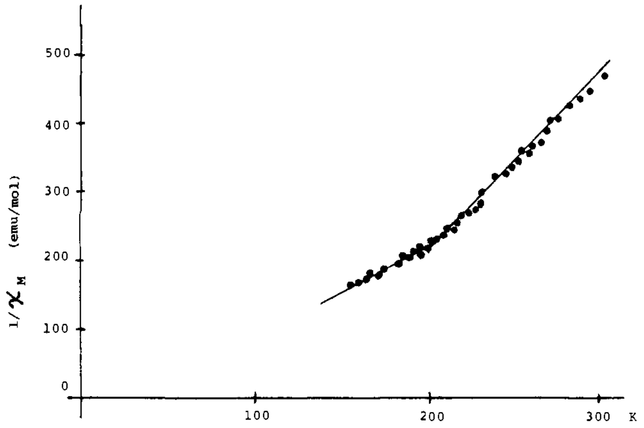


Figure 5. Magnetic susceptibility of cobalt hexaaza macrocycle complex (**5**).

at 296 K, which is rather high for one spin. On the other hand, the magnetic susceptibility of copper complex **6** is 1.53×10^{-3} emu/mol at 296 K. This value is reasonable for one spin compound. Figgis attributed the low values (1.7–2.0 μ_B) to the octahedral structure. Though the observed value lies within this range, we have no explanation for the fact that macrocycle–cobalt complex **5** has an octahedral structure. However, we may present one possible explanation for a large difference between the magnetic moment of the temperature range 140–210 K and that of the temperature range 210–296 K; that is, the cobalt ion and the hexaaza macrocycle ligand are not coplanar in the temperature range of 210–296 K. Another possible interpretation is the effect of the coordination of oxygen molecule to cobalt atom. Though the measurements were performed in a helium atmosphere, there is a possibility that the oxygen molecule coordinates to cobalt atom in preparation or sampling for measurements. However, any definite evidences in favor of either of these interpretations have not been obtained yet.

Experimental Section

Macrocycles and macrocycle-metal complexes were prepared and purified as described in previous reports.[8]

Anhydrous cupric chloride ($CuCl_2$) was prepared by a published method.

All x-ray photoelectron spectra were obtained using a JASCO ESCA-1 photoelectron spectrometer, employing Mg Kα x rays. The samples were used as fine powder dusted onto a double-side sticky tape which was mounted on a copper sample holder. Aluminum foil was used for measurements at elevated temperatures. The macrocycle-metal complexes are extremely stable: the heating and the x-ray radiation gave no visible evidence of damage of samples, and the results of gas analyses by means of a mass filter (Uthe Technology International Co.) also give no evidence of evolution of gases by decomposition. For highly hygroscopic substances, the samples were left under vacuum (1×10^{-7} Torr) for 5 h before measurements. XPS spectra were run over a 25–50-eV range for each element in the compound, and 10–20-s scans were averaged for each line. Binding energies, peak heights, and peak width at half-height were recorded in triplicate, and binding energies were read at the midway point of the full back at half-height accuracy being within ±0.20 eV. All raw binding energies were corrected to an impurity C 1s value of 284 eV. The spectra were also standardized by using a gold layer deposited over the samples under vacuum as a reference; Au $4f_{7/2}$ = 83 eV.

Magnetic susceptibilities were measured on powdered samples by a Faraday balance using Pyrex sample tubes which were calibrated, in a temperature range of 80–296 K. Low-temperature measurements were carried out by utilizing a Dewar vessel which was filled with liquid nitrogen. Pascal's law and the value of phenanthrene[15] were used to correct the molar diamagnetic term.

^1H NMR spectra were recorded on a Hitachi R-20A NMR spectrometer using trifluoroacetic acid (TFA) as a solvent and Me_4Si as an internal standard.

References and Notes

(1) J. L. Hoard, *Science*, **174**, 1295 (1971); D. A. Summerville and I. A. Cohen, *J. Am. Chem. Soc.*, **98**, 1747 (1976); C. J. Weschler, S. M. Hoffmann, and F. Basolo, *ibid.*, **97**, 5278 (1975).

(2) D. E. Goldberg and K. M. Thomas, *J. Am. Chem. Soc.*, **98**, 913 (1976); S. J. Silvers and A. Tulinsky, *ibid.*, **89**, 3331 (1967); J. W. Lauher and J. A. Ibers, *ibid.*, **95**, 5148 (1973).

(3) M. V. Zeller and R. G. Hayes, *J. Am. Chem. Soc.*, **95**, 3855 (1973); Y. Niwa, H. Kobayashi, and T. Tsuchiya, *J. Chem. Phys.*, **60**, 799 (1974).

(4) S. C. Tank, S. Koch, G. N. Weinstein, R. W. Lane, and R. H. Holm, *Inorg. Chem.*, **12**, 2589 (1973); F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974); D. P. Riley, J. A. Stone, and D. H. Busch, *ibid.*, **98**, 1753 (1976).

(5) J. E. Baldwin and J. Huff, *J. Am. Chem. Soc.*, **95**, 5757 (1973).

(6) C. K. Chang and T. G. Traylor, *J. Am. Chem. Soc.*, **95**, 8477 (1973).

(7) J. P. Collman, R. R. Gagne, T. R. Halbert, J. C. Marchon, and C. A. Reed, *J. Am. Chem. Soc.*, **95**, 7868 (1973); J. P. Collman, R. R. Gagne, and C. A. Reed, *ibid.*, **96**, 2629 (1974).

(8) S. Ogawa, T. Yamaguchi, and N. Gotoh, *J. Chem. Soc., Perkin Trans. 1*, 976 (1974); S. Ogawa, *ibid.*, 214 (1977).

(9) M. Senō and S. Tsuchiya, *J. Electron Spectrosc. Relat. Phenom.*, **8**, 165 (1976); M. Senō and S. Tsuchiya, *J. Chem. Soc., Dalton Trans.*, in press.

(10) D. C. Frost, A. Ishitani, and C. A. McDowell, *Mol. Phys.*, **24**, 861 (1972).

(11) M. Senō, S. Tsuchiya, M. Hidai, and Y. Uchida, *Bull. Chem. Soc. Jpn.*, **49**, 1184 (1976).

(12) Ray and Sen, *J. Indian Chem. Soc.*, **25**, 473 (1948).

(13) B. N. Figgis and C. M. Harris, *J. Chem. Soc.*, 855 (1959).

(14) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954).

(15) "Landolt-Börnstein Tabellen", Neue Serie, Vol. II, 2 Teil, Springer-Verlag, West Berlin, 1966.