of the amide chain while still retaining both benzophenone imine groups. This is presumably due to lack of stability of the five-coordination in the zinc(II) complex. However, in all cases, once one of the benzophenone end groups breaks off, the linear triamine chain degrades atom by atom.

The cbpS complexes, in contrast, do not show loss of H_2S to any great extent. This is in agreement with the observation that the M–S bond is considerably stronger than the M–N bond. The spectra show, first, a loss of one of the benzophenone groups and then degradation of the aliphatic chains. Although atom-by-atom degradation does occur, loss of the entire propyl group is seen to be the principal process. Also, a peak corresponding to benzophenone *N*-propylimine appears, which is not seen in the cbpN complexes. The similarity of the mass spectra of the Co– and Cu–cbpS complexes to those of the analogous salS's indicates that any differences in the behavior of the potentially coordinating sulfur atom in cbpS and salS is quite subtle. The extent of the difference between the two ligands and the reasons for it warrant closer study.

Conclusion

The structures of Cu(mbpN) and Ni(mbpN) reveal both complexes to be five-coordinate. From their spectral and magnetic properties and those of the corresponding cbpN and cbpS complexes with M = Cu(II), Ni(II) or Co(II) we predict that the latter will also be five-coordinate and that M–S, M–N bonding is general in such complexes. This prediction is supported by structural determinations of [McbpS·3-Mepy]·$^1/_2$(3-Mepy) (M = Ni(II), Co(II)), where, in each case, the thioether sulfur is coordinated to the metal. In the same way, where the properties of the two series are the same, we can postulate that thioether coordination occurs in the salX complexes. Specifically ruled out for these cases would be four-coordinated structures for Cu(II) and Co(II) and,

probably, polymeric structures for Ni(II).

References and Notes

(1) (a) University of Wollongong. (b) University of Virginia.
(2) M. Di Vaira, P. L. Orioli, and L. Sacconi, *Inorg. Chem.*, **10**, 553 (1971).
(3) M. Seleborg, S. L. Holt, and B. Post, *Inorg. Chem.*, **10**, 1501 (1971).
(4) P. C. Healy, G. M. Mockler, D. P. Freyberg, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 691 (1975).
(5) D. P. Freyberg, G. M. Mockler, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 447 (1976).
(6) R. H. Niswander, A. K. St. Clair, S. R. Edmondson, and L. T. Taylor, *Inorg. Chem.*, **14**, 478 (1975).
(7) L. W. Lane and L. T. Taylor, *J. Coord. Chem.*, **2**, 295 (1973).
(8) R. H. Niswander and L. T. Taylor, cited in ref 6.
(9) W. C. Hoyt and G. W. Everett, Jr., *Inorg. Chem.*, **8**, 2013 (1969).
(10) G. M. Mockler, G. W. Chaffey, E. Sinn, and H. Wong, *Inorg. Chem.*, **11**, 1308 (1972).
(11) G. M. Mockler and E. Sinn, to be submitted for publication.
(12) B. N. Figgis and R. H. Nyholm, *J. Chem. Soc.*, 331 (1959).
(13) D. P. Graddon and G. M. Mockler, *Aust. J. Chem.*, **21**, 617 (1968).
(14) D. P. Freyberg, G. M. Mockler, and E. Sinn, to be submitted for publication; E. M. Boge, G. M. Mockler, and E. Sinn, unpublished data.
(15) E. M. Boge, G. M. Mockler, and E. Sinn, submitted for publication.
(16) L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).
(17) L. T. Taylor and J. G. Dillard, *Inorg. Chem.*, **13**, 2620 (1974).

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Crystal and Molecular Structures of [*N*,*N'*-Bis((5-chloro-2-hydroxyphenyl)phenylmethylene)-4-thiaheptane-1,7-diamino]copper(II)

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The title complex has been synthesized and studied by single-crystal x-ray diffraction. Crystal data for Cu(cbpS), $CuCl_2SO_2N_2C_{38}H_{28}$, are as follows: space group $C2/c$, $Z = 8$, $a = 18.689$ (4) Å, $b = 13.735$ (5) Å, $c = 22.669$ (9) Å, $\beta = 100.61$ (2)°, $V = 5720$ Å^3, $R = 3.1\%$, 2606 reflections. The complex molecule contains the metal atom in a distorted square pyramid with the Cu–S bond pointing at the apex. The O_2N_2 base of the pyramid is distorted so as to give some trigonal-bipyramidal character to the geometry, the N atoms being raised above (0.07 Å) the Cu atom and the O atoms below it (0.3 Å). Although the Cu–S bond is elongated (2.686 (1) Å), it is no weaker than the Cu–N bonds in related copper Schiff base complexes. The observation of a Cu–S bond at all is unexpected from the interpretation of earlier physical data on complexes containing the same type of thioether chain in the ligand. It now appears likely that such a bond occurs in some other complexes where its existence had not previously been proposed from the available data.

Introduction

Complexes McbpX and MmbpX of the ligands H_2cbpX (**1**,

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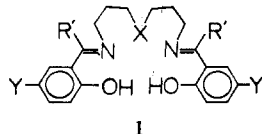
with R' = C_6H_5, Y = Cl) and H_2mbpX (**1**, with R' = C_6H_5, Y = CH_3) have been found to contain MX bonds when M = Co(II) or Ni(II) and X = S[2] and when M = Ni, Cu,[3] or Zn[4]

and X = NH. Such a bond has also been postulated for the case M = Cu(II) and X = S.[5] On the other hand, for the unsubstituted MsalX complexes (**1**, R' = Y = H), the structures were previously proposed to be four-coordinated and hence presumably square planar for M = Cu(II) and tetrahedral for M = Co(II) and X = S.[6-8] The Ni(II) analogues were proposed to be polymeric,[8] like the NiSalR complexes[9] (SalRH$_2$ is **2** with R' = Y = H). No Ni–X bond would then be required to explain the magnetic or spectral properties. However, there is evidence that the SalR, cbpX (X = NH, S), cbpR (**2**, R' = C_6H_5, Y = Cl), and mbpR (**2**, R' = C_6H_5,
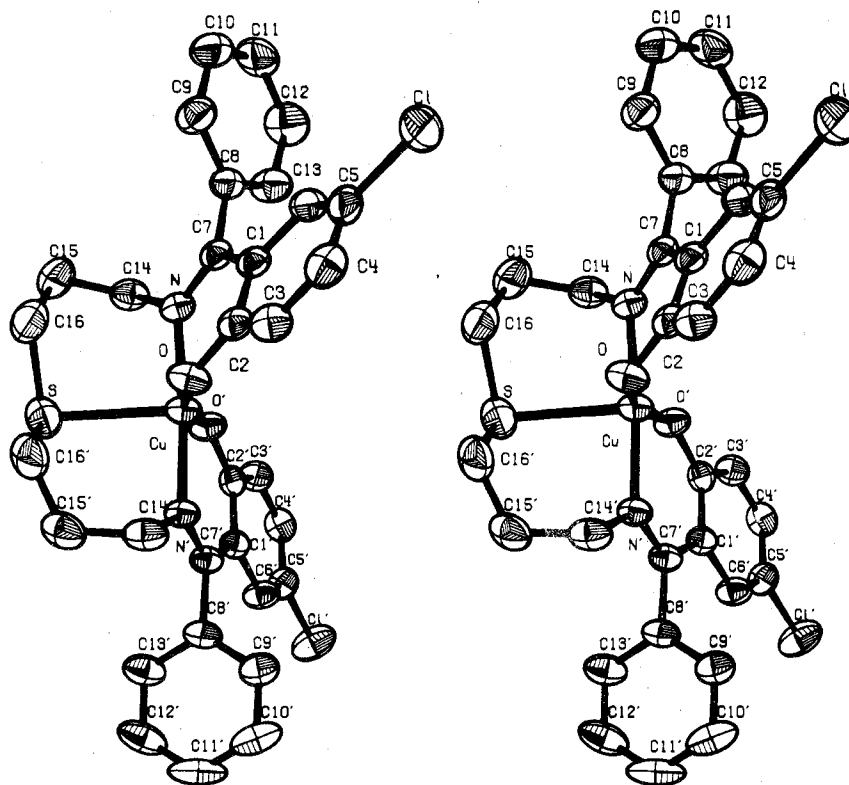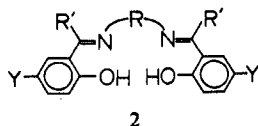
Figure 1.

2

$Y = CH_3$) complexes of nickel(II) are nonpolymeric.[2,10,11]

The Cu–X bond is significantly elongated in Cu(mbpN) (2.37 Å, compared with 2.04 Å in the Ni(II) analogue). A very weak or nonexistent Cu–S bonding interaction might be expected from this observation, since a weaker interaction of copper(II) with a thioether donor than with a corresponding amine is quite plausible. The frequent occurrence of four-coordinated copper(II) makes this a reasonable expectation. Thus, Cu(cbpS) would appear to present the best chance of observing a complex of a type **1** ligand with no M–X bond, if such complexes exist. We show that the Cu–S bond exists in this complex and that it is no weaker than the Cu–N bond in Cu(mbpN).

Experimental Section

The ligand H_2cbpS and its copper(II) complex were prepared as described previously.[5] Black crystals of the complex were grown by slow evaporation of a benzene solution.

Crystal data for Cu(cbpS), $CuCl_2SO_2N_2C_{38}H_{28}$: mol wt 639, space group $C2/c$, $Z = 8$, $a = 18.689$ (4) Å, $b = 13.735$ (5) Å, $c = 22.669$ (9) Å, $\beta = 100.61$ (2)°, $V = 5720$ Å³, $\rho_{calcd} = 1.49$ g cm⁻³, $\rho_{obsd} = 1.48$ g cm⁻³, $\mu(Mo\ K\alpha) = 10.9$ cm⁻¹; black crystal, dimensions with distances in mm from centroid: (111) 0.07, (III) 0.07, (1Ī1) 0.06, (Ī11) 0.06, (110) 0.085, (Ī10) 0.085, (001) 0.15, (00Ī) 0.15. Density was measured by flotation (KI).

The Enraf-Nonius program SEARCH was used to obtain 15 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of the Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation

from a highly oriented graphite crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $0° < 2\theta < 46°$. Scan widths (SW) were calculated from the formula $SW = A + B \tan \theta$ where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to $K\alpha_1$ and $K\alpha_2$ splitting. The values of A and B were 0.6 and 0.3°, respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as $NC = TOT - 2(BG1 + BG2)$ where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 20 counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored at 100 reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. After averaging of the intensities of equivalent reflections, the data were reduced to 4105 independent intensities of which 2606 had $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[12] These data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structure. The positions of the metal and the ligand donor atoms were obtained from both a three-dimensional Patterson function and from MULTAN 74.[13] The positions of the remaining nonhydrogen atoms were determined from a Fourier difference function.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were then taken as $[2F_o/\sigma(F_o^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber,[14] and those for hydrogen, from Stewart et al.[15] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c using the values of Cromer and Ibers[16] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. The principal programs used have been described.[5]

Anisotropic temperature factors were introduced for all nonhydrogen atoms. Hydrogen atoms were inserted in their calculated positions and included in the refinement for three cycles and subsequently held

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for Cu(cbpS)[a]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	0.41598 (3)	0.71867 (3)	0.36021 (2)	0.00228 (1)	0.00274 (2)	0.001194 (9)	−0.00086 (4)	0.00040 (2)	0.00003 (3)
Cl	0.74682 (6)	0.86926 (9)	0.54257 (5)	0.00214 (4)	0.00674 (8)	0.00264 (3)	−0.00016 (9)	−0.00010 (6)	−0.00204 (8)
Cl′	0.40081 (8)	0.42853 (9)	0.09042 (5)	0.00596 (5)	0.00544 (7)	0.00155 (2)	0.00138 (11)	0.00185 (5)	−0.00128 (7)
S	0.27961 (6)	0.76622 (9)	0.37113 (5)	0.00253 (4)	0.00612 (8)	0.00212 (3)	−0.0004 (1)	0.00128 (5)	−0.00007 (8)
O	0.4572 (1)	0.7131 (2)	0.4452 (1)	0.00280 (9)	0.0039 (1)	0.00110 (5)	−0.0020 (2)	0.0002 (1)	0.0002 (2)
O′	0.4089 (1)	0.7281 (2)	0.2756 (1)	0.00291 (9)	0.0028 (1)	0.00121 (5)	−0.0005 (2)	0.0007 (1)	0.0001 (2)
N	0.4408 (2)	0.8607 (2)	0.3652 (1)	0.0023 (1)	0.0026 (2)	0.00129 (7)	−0.0000 (2)	0.0006 (1)	−0.0001 (2)
N′	0.3841 (2)	0.5799 (2)	0.3549 (1)	0.0023 (1)	0.0028 (2)	0.00123 (7)	−0.0010 (2)	0.0007 (1)	0.0000 (2)
C(1)	0.5470 (2)	0.8395 (3)	0.4417 (2)	0.0021 (1)	0.0028 (2)	0.00112 (8)	−0.0002 (3)	0.0010 (2)	−0.0008 (2)
C(2)	0.5207 (2)	0.7534 (3)	0.4655 (2)	0.0022 (1)	0.0034 (2)	0.00093 (7)	−0.0000 (3)	0.0008 (2)	−0.0008 (2)
C(3)	0.5662 (2)	0.7099 (3)	0.5156 (2)	0.0028 (1)	0.0039 (2)	0.00120 (8)	−0.0004 (3)	0.0007 (2)	−0.0001 (3)
C(4)	0.6333 (2)	0.7444 (3)	0.5382 (2)	0.0027 (1)	0.0050 (3)	0.00108 (8)	0.0012 (3)	0.0001 (2)	−0.0007 (3)
C(5)	0.6594 (2)	0.8262 (3)	0.5130 (3)	0.0019 (1)	0.0046 (2)	0.00147 (9)	0.0006 (3)	0.0003 (2)	−0.0016 (3)
C(6)	0.6174 (2)	0.8728 (3)	0.4663 (2)	0.0023 (1)	0.0030 (2)	0.00157 (9)	−0.0007 (3)	0.0009 (2)	−0.0007 (2)
C(7)	0.5013 (2)	0.8956 (3)	0.3946 (2)	0.0021 (1)	0.0029 (2)	0.00115 (8)	−0.0002 (3)	0.0012 (2)	−0.0008 (2)
C(8)	0.5278 (2)	0.9952 (3)	0.3809 (2)	0.0021 (1)	0.0029 (2)	0.00144 (8)	−0.0005 (3)	0.0004 (2)	−0.0000 (2)
C(9)	0.5279 (2)	1.0739 (3)	0.4192 (2)	0.0034 (2)	0.0037 (2)	0.00186 (9)	−0.0006 (3)	0.0023 (2)	−0.0005 (3)
C(10)	0.5563 (3)	1.1620 (3)	0.4062 (2)	0.0035 (2)	0.0036 (2)	0.00271 (12)	−0.0016 (4)	0.0018 (2)	−0.0014 (3)
C(11)	0.5856 (2)	1.1718 (3)	0.3548 (2)	0.0032 (2)	0.0036 (2)	0.00324 (13)	−0.0019 (4)	0.0016 (2)	0.0012 (3)
C(12)	0.5871 (3)	1.0943 (4)	0.3174 (2)	0.0044 (2)	0.0063 (3)	0.00196 (10)	−0.0022 (4)	0.0028 (2)	0.0010 (3)
C(13)	0.5569 (2)	1.0066 (3)	0.3301 (2)	0.0036 (2)	0.0041 (2)	0.00170 (9)	−0.0017 (4)	0.0017 (2)	−0.0006 (3)
C(14)	0.3854 (2)	0.9232 (3)	0.3291 (2)	0.0027 (1)	0.0031 (2)	0.00162 (9)	−0.0003 (3)	−0.0000 (2)	0.0007 (3)
C(15)	0.3302 (2)	0.9566 (3)	0.3665 (2)	0.0032 (2)	0.0044 (3)	0.00272 (12)	0.0023 (4)	0.0011 (2)	−0.0002 (3)
C(16)	0.3088 (3)	0.8816 (3)	0.4099 (2)	0.0036 (2)	0.0051 (3)	0.00269 (11)	0.0014 (4)	0.0024 (2)	−0.0004 (3)
C(1′)	0.3945 (2)	0.5570 (3)	0.2503 (2)	0.0018 (1)	0.0030 (2)	0.00114 (8)	−0.0001 (3)	0.0004 (2)	0.0003 (2)
C(2′)	0.4071 (2)	0.6561 (3)	0.2376 (2)	0.0015 (1)	0.0037 (2)	0.00115 (8)	0.0001 (3)	0.0003 (2)	0.0003 (2)
C(3′)	0.4156 (2)	0.6797 (3)	0.1783 (2)	0.0026 (1)	0.0038 (2)	0.00148 (9)	−0.0006 (3)	0.0007 (2)	0.0006 (3)
C(4′)	0.4140 (2)	0.6117 (3)	0.1347 (2)	0.0025 (1)	0.0053 (3)	0.00108 (8)	−0.0003 (3)	0.0011 (2)	0.0009 (3)
C(5′)	0.4025 (2)	0.5151 (3)	0.1475 (2)	0.0026 (1)	0.0046 (2)	0.00112 (8)	0.0003 (3)	0.0011 (2)	−0.0007 (3)
C(6′)	0.3925 (2)	0.4882 (3)	0.2031 (2)	0.0032 (1)	0.0030 (2)	0.00142 (9)	−0.0007 (3)	0.0012 (2)	0.0003 (2)
C(7′)	0.3796 (2)	0.5238 (3)	0.3082 (2)	0.0020 (1)	0.0027 (2)	0.00127 (8)	−0.0005 (3)	0.0003 (2)	0.0004 (2)
C(8′)	0.3549 (2)	0.4194 (3)	0.3099 (2)	0.0027 (1)	0.0032 (2)	0.00097 (8)	−0.0016 (3)	0.0003 (2)	0.0002 (2)
C(9′)	0.4048 (2)	0.3438 (3)	0.3181 (2)	0.0031 (2)	0.0038 (2)	0.00141 (9)	−0.0002 (3)	0.0006 (2)	0.0003 (2)
C(10′)	0.3809 (3)	0.2483 (3)	0.3152 (2)	0.0055 (2)	0.0034 (2)	0.00175 (10)	0.0010 (4)	0.0000 (3)	−0.0003 (3)
C(11′)	0.3080 (3)	0.2279 (3)	0.3044 (2)	0.0062 (2)	0.0035 (2)	0.00178 (10)	−0.0043 (4)	−0.0009 (3)	0.0007 (3)
C(12′)	0.2588 (3)	0.3020 (3)	0.2971 (2)	0.0033 (2)	0.0064 (3)	0.00221 (11)	−0.0045 (4)	−0.0012 (2)	0.0007 (3)
C(13′)	0.2813 (2)	0.3976 (3)	0.2993 (2)	0.0030 (2)	0.0043 (3)	0.00179 (10)	−0.0017 (4)	−0.0005 (2)	0.0005 (3)
C(14′)	0.3626 (2)	0.5422 (3)	0.4106 (2)	0.0039 (2)	0.0037 (2)	0.00121 (8)	−0.0017 (3)	0.0012 (2)	0.0004 (2)
C(15′)	0.2878 (2)	0.5788 (3)	0.4190 (2)	0.0038 (2)	0.0060 (3)	0.00164 (9)	−0.0033 (4)	0.0022 (2)	−0.0003 (3)
C(16′)	0.2824 (2)	0.6842 (4)	0.4358 (2)	0.0033 (2)	0.0074 (3)	0.00205 (10)	−0.0014 (4)	0.0028 (2)	−0.0008 (3)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
H(3)	0.546 (2)	0.658 (3)	0.533 (2)	3.3 (9)	H(3′)	0.422 (2)	0.744 (3)	0.172 (2)	4.0 (10)
H(4)	0.661 (2)	0.713 (3)	0.568 (2)	3.1 (9)	H(4′)	0.422 (2)	0.629 (3)	0.097 (2)	4.5 (10)
H(6)	0.636 (2)	0.927 (3)	0.452 (1)	2.6 (8)	H(6′)	0.383 (2)	0.426 (3)	0.210 (2)	3.9 (10)
H(9)	0.508 (2)	1.066 (3)	0.451 (2)	4.0 (10)	H(9′)	0.454 (2)	0.362 (3)	0.325 (2)	4.2 (10)
H(10)	0.557 (2)	1.212 (3)	0.435 (2)	4.8 (10)	H(10′)	0.412 (2)	0.199 (3)	0.319 (2)	5.0 (11)
H(11)	0.604 (2)	1.228 (3)	0.346 (2)	4.6 (10)	H(11′)	0.291 (2)	0.166 (3)	0.301 (2)	4.6 (10)
H(12)	0.606 (2)	1.102 (3)	0.285 (2)	4.6 (10)	H(12′)	0.212 (2)	0.290 (3)	0.293 (2)	4.4 (10)
H(13)	0.559 (2)	0.953 (3)	0.306 (2)	4.2 (10)	H(13′)	0.249 (2)	0.445 (3)	0.294 (2)	3.7 (10)
H(141)	0.405 (2)	0.978 (3)	0.312 (2)	3.7 (9)	H(143)	0.364 (2)	0.474 (3)	0.410 (2)	3.6 (9)
H(142)	0.363 (2)	0.884 (3)	0.294 (2)	4.1 (10)	H(144)	0.400 (2)	0.567 (3)	0.443 (2)	3.7 (9)
H(151)	0.288 (2)	0.982 (3)	0.341 (2)	4.5 (10)	H(153)	0.252 (2)	0.568 (3)	0.383 (2)	4.7 (10)
H(152)	0.349 (2)	1.005 (3)	0.391 (2)	3.9 (10)	H(154)	0.276 (2)	0.548 (3)	0.451 (2)	4.2 (10)
H(161)	0.263 (2)	0.899 (3)	0.420 (2)	5.9 (12)	H(163)	0.329 (2)	0.702 (3)	0.468 (2)	4.1 (10)
H(162)	0.352 (2)	0.871 (3)	0.442 (2)	4.5 (10)	H(164)	0.239 (2)	0.698 (3)	0.450 (2)	5.1 (11)

[a] The form of the anisotropic thermal parameter is $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

fixed. The model converged with $R = 3.1$, $R_w = 3.7\%$. The largest parameter shift at convergence was one-tenth of its estimated standard deviation. The error in a observation of unit weight is 1.6. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 3.5\%$; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference function was featureless. Tables of the observed structure factors are available.[17]

X-Band ESR spectra were measured on a Varian E109 spectrometer with E102 microwave bridge.

Results and Discussion

Final positional and thermal parameters are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1 is a stereoscopic pair view of Cu(cbpS) while Figure 2 shows the molecular packing in the unit cell.

The complex consists of well-separated (Table IV, Figure 2) monomeric molecules, the closest intermolecular approach (3.32 Å) being between a ligand oxygen and a phenyl carbon atom. The ligand environment about the metal is approximately square pyramidal, with some distortion toward trigonal-bipyramidal geometry. The copper atom lies close (0.11 Å) to the O_2N_2 base of the square pyramid (plane I in Table
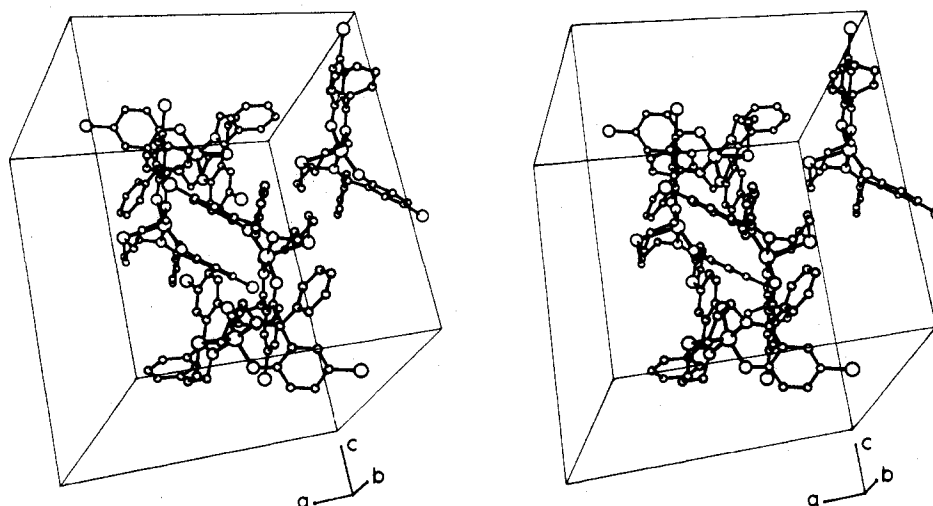
Figure 2.

Table II. Bond Distances (Å) for Cu(cbpS)

Cu–S	2.686 (1)	C(8)–C(13)	1.371 (4)
Cu–O	1.941 (2)	C(9)–C(10)	1.375 (5)
Cu–O'	1.902 (2)	C(10)–C(11)	1.381 (5)
Cu–N	2.004 (3)	C(11)–C(12)	1.364 (5)
Cu–N'	1.993 (3)	C(12)–C(13)	1.383 (5)
S–C(16)	1.845 (4)	C(14)–C(15)	1.522 (5)
S–C(16')	1.842 (4)	C(15)–C(16)	1.529 (5)
O–C(2)	1.313 (4)	C(1')–C(2')	1.420 (4)
O'–C(2')	1.307 (4)	C(1')–C(6')	1.422 (4)
N–C(7)	1.293 (4)	C(1')–C(7')	1.463 (4)
N'–C(7')	1.299 (4)	C(2')–C(3')	1.421 (4)
N–C(14)	1.473 (4)	C(3')–C(4')	1.356 (5)
N'–C(14')	1.487 (4)	C(4')–C(5')	1.383 (5)
Cl–C(5)	1.751 (3)	C(5')–C(6')	1.361 (4)
Cl'–C(5')	1.752 (3)	C(7')–C(8')	1.510 (4)
C(1)–C(2)	1.424 (4)	C(8')–C(9')	1.385 (5)
C(1)–C(6)	1.408 (4)	C(8')–C(13')	1.385 (5)
C(1)–C(7)	1.459 (4)	C(9')–C(10')	1.384 (5)
C(2)–C(3)	1.418 (4)	C(10')–C(11')	1.368 (6)
C(3)–C(4)	1.350 (5)	C(11')–C(12')	1.361 (6)
C(4)–C(5)	1.387 (5)	C(12')–C(13')	1.376 (5)
C(5)–C(6)	1.357 (5)	C(14')–C(15')	1.529 (5)
C(7)–C(8)	1.507 (4)	C(15')–C(16')	1.506 (5)
C(8)–C(9)	1.387 (4)		

Table III. Bond Angles (deg) for Cu(cbpS)

S–Cu–O	97.36 (7)	O–C(2)–C(3)	118.2 (3)
S–Cu–O'	100.67 (7)	C(1)–C(2)–C(3)	117.1 (3)
S–Cu–N	88.39 (8)	C(2)–C(3)–C(4)	122.3 (3)
S–Cu–N'	87.73 (8)	C(3)–C(4)–C(5)	120.0 (3)
O–Cu–O'	160.91 (9)	Cl–C(5)–C(4)	119.4 (3)
O–Cu–N	86.4 (1)	Cl–C(5)–C(6)	120.2 (3)
O–Cu–N'	94.7 (1)	C(4)–C(5)–C(6)	120.4 (3)
O'–Cu–N	87.9 (1)	C(1)–C(6)–C(5)	121.3 (3)
O'–Cu–N'	92.3 (1)	N–C(7)–C(1)	121.3 (3)
N–Cu–N'	176.1 (1)	N–C(7)–C(8)	121.3 (3)
Cu–S–C(16)	92.9 (1)	C(1)–C(7)–C(8)	117.4 (3)
Cu–S–C(16')	92.1 (1)	C(7)–C(8)–C(9)	122.8 (3)
C(16)–S–C(16')	100.6 (1)	C(7)–C(8)–C(13)	118.3 (3)
Cu–O–C(2)	119.9 (2)	C(9)–C(8)–C(13)	118.8 (3)
Cu–O'–C(2')	126.9 (2)	C(8)–C(9)–C(10)	120.5 (3)
Cu–N–C(7)	124.2 (2)	C(9)–C(10)–C(11)	119.7 (3)
Cu–N–C(14)	113.8 (2)	C(10)–C(11)–C(12)	120.3 (3)
C(7)–N–C(14)	121.9 (3)	C(11)–C(12)–C(13)	119.7 (4)
Cu–N'–C(7')	126.2 (2)	C(8)–C(13)–C(12)	121.0 (3)
Cu–N'–C(14')	113.9 (2)	N–C(14)–C(15)	110.2 (3)
C(7')–N'–C(14')	119.9 (3)	C(14)–C(15)–C(16)	116.1 (3)
C(2)–C(1)–C(6)	118.9 (3)	S–C(16)–C(15)	111.2 (3)
C(2)–C(1)–C(7)	121.3 (3)	C(2')–C(1')–C(6')	117.9 (3)
C(6)–C(1)–C(7)	119.8 (3)	C(2')–C(1')–C(7')	123.0 (3)
O–C(2)–C(1)	124.7 (3)	C(6')–C(1')–C(7')	119.0 (3)
O'–C(2')–C(1')	125.3 (3)	C(7')–C(8')–C(9')	120.9 (3)
O'–C(2')–C(3')	117.2 (3)	C(7')–C(8')–C(13')	120.0 (3)
C(1')–C(2')–C(3')	117.5 (3)	C(9')–C(8')–C(13')	118.9 (3)
C(2')–C(3')–C(4')	122.8 (3)	C(8')–C(9')–C(10')	120.0 (4)
C(3')–C(4')–C(5')	119.5 (3)	C(9')–C(10')–C(11')	120.4 (4)
Cl'–C(5')–C(4')	118.7 (3)	C(10')–C(11')–C(12')	119.7 (4)
Cl'–C(5')–C(6')	120.9 (3)	C(11')–C(12')–C(13')	121.0 (4)
C(4')–C(5')–C(6')	120.5 (3)	C(8')–C(13')–C(12')	120.0 (4)
C(1')–C(6')–C(5')	121.9 (3)	N'–C(14')–C(15')	112.8 (3)
N'–C(7')–C(1')	123.5 (3)	C(14')–C(15')–C(16')	117.0 (3)
N'–C(7')–C(8')	121.2 (3)	S–C(16')–C(15')	112.4 (3)
C(1')–C(7')–C(8')	115.3 (3)		

Table IV. Closest Intermolecular Contacts

Mol 1	Mol 2	Dist, Å	Symmetry transformation
Cl	C(4')	3.434 (4)	$1/2 + x, 1^{1}/_{2} - y, 1/2 + z$
O'	C(3')	3.320 (4)	$1 - x, y, 1/2 - z$
O'	C(12')	3.416 (4)	$1/2 - x, 1/2 + y, 1/2 - z$
C(2)	C(4')	3.385 (4)	$1 - x, y, 1/2 - z$
C(4)	C(10')	3.385 (5)	$1 - x, 1 - y, 1 - z$
C(2')	C(2')	3.415 (6)	$1 - x, y, 1/2 - z$

V), but this base is distorted from planarity with the nitrogen atoms raised out of the plane, above (0.07 Å) the metal atom while the oxygen atoms are below (0.30 Å) the metal. The angles O–Cu–O, O–Cu–S, and O'–Cu–S are 160.9, 97.4, and 100.7°, respectively, compared to an undistorted square-pyramidal arrangement which requires 180, 90, and 90°, respectively, and trigonal-bipyramidal geometry which requires 120° for all three angles. The N–Cu–N' angle is 176.1° while both idealized geometries require 180°. The Cu–S bond is tilted slightly away from the axis of the approximate square pyramid, mainly in the O_2S plane, being 1.7° away from the bisector of the O–Cu–O' angle. The other main feature of molecular distortion is the difference between the coplanar (conjugated) ligand fragment O, N, C1–C7 (plane VI in Table V) and its counterpart O', N', C(1')–C(7') (plane VII). Plane VII passes close to the Cu atom, and its phenyl ring at C(7') (plane V) is approximately orthogonal to it. This feature is common to a series of related complexes. On the other hand, the O, N, C(1)–C(7) plane is bent markedly away from the metal atom, but with this distortion, its phenyl ring (plane V) is not required to be as nearly orthogonal.

The Cu–S bond (2.686 Å) is elongated compared to strong Cu–S bonds and M–S bonds in general (Table VI). Five-coordinated copper(II) complexes normally contain one bond markedly longer than the other four, and the simplest measure

of the elongation is given by the difference between the long bond and the average short bond, after allowing for atomic size. In the dimeric Cu(dtc) complex (Table VI)[18] the four short bonds average 2.313 Å, while the fifth bond is extra long at 2.851 Å. If we assume 2.313 Å as the lower limit "normal"

Table V. Coefficients of Least-Squares Planes for $AX + BY + CZ = D$

Plane	Atoms in plane	A	B	C	D	Distances from plane, Å
I	O, O', N, N'	0.887	−0.234	−0.398	2.838	O, 0.16; O', 0.18; N, −0.18; N', −0.16; Cu, −0.11
II	C(1)–C(6)	0.456	−0.508	−0.731	−7.531	C(1), −0.01; C(2), 0.02; C(3), −0.01; C(4), 0; C(5), 0.01; C(6), 0; Cu, 0.88
III	C(8)–C(13)	−0.920	0.316	−0.234	−8.209	C(8), 0; C(9), −0.01; C(10), 0; C(11), 0.01; C(12), −0.01; C(13), 0.01; Cu, 0.91
IV	C(1')–C(6')	0.986	−0.143	−0.088	6.719	C(1'), 0; C(2'), 0.01; C(3'), −0.01; C(4'); 0; C(5'), 0.01; C(6'), −0.01; Cu, 0.32
V	C(8')–C(13')	0.167	−0.012	−0.986	−5.558	C(8'), 0; C(9'), 0; C(10'), 0; C(11'), 0; C(12'), −0.01; C(13'), 0; Cu, −0.93
VI	O, N, C(1)–C(7)	0.464	−0.489	−0.739	−7.313	O, 0.02; N, 0.05; C(1), 0; C(2), 0.01; C(3), −0.04; C(4), −0.01; C(5), 0.03; C(6), 0.03; C(7), −0.09; Cu, 0.86
VII	O', N', C(1')–C(7')	0.986	−0.149	−0.079	6.705	O', −0.01; N', 0.03; C(1'), 0.02; C(2'), 0.02; C(3'), −0.01; C(4'), −0.01; C(5'), 0.01; C(6'), 0.01; C(7'), −0.05; Cu, 0.34

Angles between Planes, Deg

I,II	I,III	I,IV	I,V	I,VI	I,VII	II,III	II,IV	II,V	II,VI	II,VII
35.5	142.8	19.5	57.1	35.0	19.8	114.1	54.1	36.6	1.2	54.4

III,IV	III,V	III,VI	III,VII	IV,V	IV,VI	IV,VII	V,VI	V,VII	VI,VII
158.6	85.8	114.1	159.2	75.4	53.7	0.6	35.7	75.9	54.0

Table VI. Some Metal–Sulfur Bond Distances

Complex	Bond(s)	Length, Å	Ref
Cu(tam)$_4$Cl[a]	Cu–S	2.343 (5)	20
Cu(dtc)[b]	Cu–S	2.297 (2), 2.301 (2) 2.317 (2), 2.339 (2) 2.851 (2)[c]	19
3, M = Cu	Cu–S	2.303 (1)	19
3, M = Ni	Ni–S	2.176 (2)	19
Ni(dtp)$_2$[d]	Ni–S	2.230 (4), 2.236 (4)	21
Ni(dtp)$_2$(py)$_2$	Ni–S	2.482 (4), 2.523 (3)	22
Ni(cbpS)mpy,[e] Ni(cbpS)py	Ni–S	2.484 (1)	2
Co(cbpS)mpy	Co–S	2.537 (1)	2

[a] tam = thioacetamide. [b] dtc = N,N-diethyldithiocarbamate.
[c] Elongated fifth bond. [d] dtp = O,O'-diethyldithiophosphate.
[e] mpy = 3-methylpyridine.

distance for a short Cu–S bond in a five-coordinated complex, as in Cu(dtc), then a slightly shortened Cu–S bond would be expected in a four-coordinated complex such as **3** (2.303 Å,
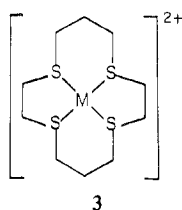

3

Table VI).[19] The Cu–S bond in the five-coordinated Cu(cbpS) complex may then be considered as elongated by 0.37 Å. If 2.0 Å is taken as the "normal" Cu–N distance (as in Table II), then the Cu–N bond at 2.37 Å in Cu(cbpN) is elongated to about the same extent as the Cu(cbpS) Cu–S bond. Thus the Cu–X bonds in the two Cu(cbpX) complexes are not significantly different in chemical character.

The close resemblance of the ESR spectra for Cu(cbpS) (Table VII) and Cu(cbpN)[3] demonstrates the similarity of the complexes. The unpaired electron is in the N_2O_2 plane in square-pyramidal geometry and along the N–Cu–N' axis in trigonal-bipyramidal. The real Cu(cbpX) geometries, square pyramidal distorted toward trigonal bipyramidal, therefore imply minimal electron spin density on the X donor atom. This is compatible with the observation of negligible ligand hyperfine interaction for this atom in the Cu(cbpN) complex,[3,4] though the spinless ^{32}S nucleus eliminates this possibility, in any case, for Cu(cbpS). In this case, ESR data resemble the electronic and mass spectral data in failing to discriminate

Table VII. ESR Parameters

Medium	Temp, K	Parameters ($g \pm 0.005, A \pm 2$ G)[a]
CH$_2$Cl$_2$ soln	295	$g_{av} = 2.111, A_{av} = 76$ G, $A_N = 11$G
Frozen CH$_2$Cl$_2$ soln	77	$g_\parallel = 2.240,$ A$_\parallel = 178$ G $g_\perp = 2.047,$ A$_\perp = 25$ G[b]

[a] Mean A for ^{63}Cu and ^{65}Cu. [b] $g_\perp = \frac{1}{2}(3g_{av} - g_\parallel); A_\perp = \frac{1}{2}(3A_{av} - A_\parallel)$.

between the geometrical possibilities or even to test for the existence of a Cu–S bond.

The Cu–S bond in Cu(cbpS) is normal from comparison with related Schiff base complexes.[3,4,11] As in the case of related Schiff base ligands,[2,11] the Cu–X bond in Cu(cbpS) is slightly elongated when compared to M–X bonds in related Ni(II) and Co(II) complexes such as Ni(cbpS)py (2.48 Å) and Co(cbpS)mpy (2.54 Å). The existence of a Cu–S bond could not be predicted but appeared likely from spectral data in the closely related[5] CuSalS. X-ray crystallography has not only proved superior to the spectroscopic techniques but also essential in resolving this structural question.

Registry No. Cu(cbpS), 62520-81-4.

Supplementary Material Available: Listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of Virginia. (b) University of Wollongong.
(2) E. M. Boge, G. M. Mockler, and E. Sinn, *Inorg. Chem.*, **16**, 467 (1977).
(3) P. C. Healy, G. M. Mockler, D. P. Freyberg, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 691 (1975).
(4) D. P. Freyberg, G. M. Mockler, and E. Sinn, *J. Chem. Soc., Dalton Trans.*, 447 (1976).
(5) E. M. Boge, D. P. Freyberg, E. Kokot, G. M. Mockler, and E. Sinn, *Inorg. Chem.*, preceding paper in this issue.
(6) L. W. Lane and L. T. Taylor, *J. Coord. Chem.*, **2**, 295 (1973); L. T. Taylor and J. G. Dillard, *Inorg. Chem.*, **13**, 2620 (1974).
(7) R. H. Niswander, A. K. St. Clair, S. R. Edmondson, and L. T. Taylor, *Inorg. Chem.*, **14**, 478 (1975).
(8) R. H. Niswander and L. T. Taylor, unpublished work, cited in ref 6.
(9) W. C. Hoyt and G. W. Everett, Jr., *Inorg. Chem.*, **8**, 2013 (1969).
(10) G. M. Mockler, G. W. Chaffey, E. Sinn, and H. Wong, *Inorg. Chem.*, **11**, 1308 (1972).
(11) G. M. Mockler and E. Sinn, to be submitted for publication.
(12) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(13) P. Main, M. M. Woolfson, L. Lessinger, G. Germain, and J.-P. DeClerq, "MULTAN 74"; G. Germain, P. Main, and M. M. Woolfson, *Acta*

Crystallogr., Sect. A, **27,** 368 (1971).
(14) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Kynoch Press, Birmingham, England, 1974, section 2.2.
(15) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.,* **42,** 3175 (1975).
(16) D. T. Cromer and J. A. Ibers, ref 14, section 2.3.
(17) Supplementary material.

(18) M. Bonamico, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.,* **19,** 886 (1965).
(19) P. H. Davis, L. K. White, and R. L. Belford, *Inorg. Chem.,* **14,** 1753 (1975).
(20) M. D. Glick, D. P. Gavel, L. L. Daddario, and D. B. Rorabacher, *Inorg. Chem.,* **15,** 1190 (1976).
(21) J. F. McConnell and V. Kastalsky, *Acta Crystallogr.,* **22,** 853 (1967).
(22) P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.,* **10,** 541 (1971).

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Studies Involving Nitrogen–Oxygen Donor Macrocyclic Ligands. 3. Cobalt(II) Complexes of Cyclic Diimine Ligands Derived from Salicylaldehyde and 5-Chloro-2-hydroxybenzophenone. X-Ray Structure Determination of cis-Co(C$_{19}$H$_{20}$N$_2$O$_2$)(NCS)$_2$[1]

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The interaction of cobalt(II) with three 14- or 15-membered macrocyclic ligands each incorporating two ether oxygen and two imine nitrogen donor atoms has been investigated. A range of cobalt(II) complexes with metal to macrocycle ratios of 1:1 have been isolated and these are either five- or six-coordinate. For one ligand, two isomeric thiocyanate complexes Co(C$_{19}$H$_{20}$N$_2$O$_2$)(NCS)$_2$ were isolated—orange and purple forms. Physical measurements indicate that these isomers are trans- and cis-octahedral forms. The purple isomer crystallizes in the monoclinic space group $P2_1/c$ with cell dimensions of $a = 8.299$ (3) Å, $b = 18.538$ (5) Å, $c = 14.750$ (4) Å, and $\beta = 100.90$ (5)°. The crystal structure was determined using 1208 four-circle diffractometer data with $I_{obsd} \geq 3\sigma(I)$ and refined to conventional and weighted residuals of 0.058 and 0.059. In this complex the macrocycle is folded, giving a β-cis configuration and, with two N-bonded thiocyanate anions, defines an irregular octahedron of donors about the cobalt(II) ion.

The chemistry of macrocyclic ligands can be divided into two major parts. The first of these incorporate ligands of the "crown" polyether type[3]. Such ligands generally show high affinity for many alkali metal or alkaline earth ions but coordinate much less strongly to transition metal ions. In contrast, a large number of macrocyclic ligands (both naturally occurring and synthetic) which contain four nitrogen donors are now known[4] and these are usually excellent complexing agents toward most transition metal ions, but poorer ligands toward many nontransition ions such as those of groups 1A and 2A.

As a continuation of the study of the complexing behavior of ligands which are intermediate structurally between the above two categories[1,5], we now report an investigation of the interaction of cobalt(II) with the macrocycles I, II, and III.

I: O-en-N-tn

II, R = H: Cl$_2$Ph$_2$-O-en-N-en
III, R = CH$_3$: Cl$_2$Ph$_2$-O-en-N-pn

IV
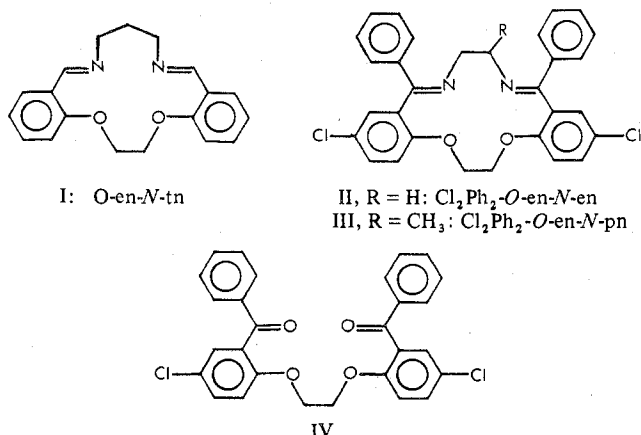
The interaction of I with nickel(II), copper(II), and cadmium(II) has been reported previously[1,5] but the related substituted macrocycles of types II and III have not been previously studied. These latter ligands were obtained by condensation of the diketone precursor IV with the corresponding diamine.

Experimental Section

Analyses for carbon, hydrogen, and nitrogen were determined by Mr. J. Kent of the Microanalytical Laboratory, University of Queensland, or by Dr. E. Challen, University of New South Wales. Cobalt was determined by atomic absorption spectroscopy. All compounds were dried over P$_4$O$_{10}$ in vacuo before analyses. The various instrumental techniques as well as the synthesis of I, O-en-N-tn, were performed as described previously.[1] We thank Dr. R. Vagg for the mass spectra.

Preparation of IV. This diketone was obtained by means of a Williamson condensation between 5-chloro-2-hydroxybenzophenone and 1,2-dibromoethane as described previously:[5] yield 40%; mp 164 °C; ¹H NMR δ 3.89 (s, CH$_2$), 6.6–7.8 (m, aromatic). Anal. Calcd for C$_{28}$H$_{20}$Cl$_2$O$_4$: C, 68.44; H, 4.10. Found: C, 68.20; H, 4.22.

General Preparation for II or III. The diketone IV and a slight excess of 1,2-diaminoethane or 1,2-diaminopropane were heated together at reflux for 1 h. The residue was dissolved in hot butanol and any insoluble material was filtered off. The solution was then taken to dryness and the crude macrocycle was recrystallized from benzene and ether. The product was dried in vacuo at 120 °C. Anal. Calcd for II, C$_{30}$H$_{24}$Cl$_2$N$_2$O$_2$: C, 69.96; H, 4.69; N, 5.43. Found: C, 70.02; H, 4.62; N, 5.55. Calcd for III, C$_{31}$H$_{26}$Cl$_2$N$_2$O$_2$: C, 70.32; H, 4.95; N, 5.29. Found: C, 70.17; H, 4.91; N, 5.21.

General Preparation for Complexes of II or III. A hot solution of II or III in benzene was added to a solution of a slight excess of cobalt salt in hot absolute alcohol. This reaction solution was boiled down on a hot plate until precipitation occurred. The product was filtered off from the boiling solution. It was washed with benzene, alcohol, and then petroleum ether.

General Preparation for Complexes of the Type [Co(O-en-N-tn)X](ClO$_4$)·nH$_2$O (n = 0 or 1). To a warm methanol solution of cobalt(II) perchlorate hexahydrate was added a mixture of O-en-N-tn and excess lithium halide in methanol. The precipitate which formed was filtered and washed with methanol.

Diiodo[5,6:14,15-dibenzo-1,4-dioxa-8,12-diazacyclopentadecane-7,12-diene)cobalt(II), Co(O-en-N-tn)I$_2$. Cobalt(II) nitrate hexa-