MOLECULES OF COPPER(II) *l*-SPARTEINE DINITRATE ARE MIXED FOUR- AND FIVE-COORDINATE IN ONE CRYSTALLINE PHASE AND ONLY FOUR-COORDINATE IN ANOTHER

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A neutral complex of Cu(II) with the chiral bidentate nitrogen-chelating alkaloid (-)-sparteine, with nitrate groups occupying the remaining coordination sites, has been prepared and characterized. Solution conductivity measurements indicate that both nitrate groups are coordinated to copper to give a neutral molecule. Optical and electron-spin-resonance spectra in toluene/CHCl$_3$, did not show a clear picture of the coordination geometry. A frozen-glass ESR spectrum showed the same evidence for mixed species, with the predominant species characterized by a very low A$_{11}$ value of 118 G. Crystals 1 and 2 of Cu(C$_{15}$H$_{26}$N$_2$)(NO$_3$)$_2$ were grown by two methods: 1 at 25°C from saturated acetonitrile, and 2 at 5°C from ethanol/dichloromethane under CCl$_4$ vapor. Their structures were determined by X-ray crystallography. Crystals 1 were monoclinic, space group P2$_1$, with a = 7.851(6), b = 14.408(10), c = 16.079(10) Å, β = 97.93(6)°, V = 1801(2) Å and Z = 4. Crystals 2 were orthorhombic, space group P2$_1$2$_1$2$_1$, with a = 7.863(4), b = 12.410(4), c = 18.050(6)Å, V = 1761(1) Å^3 and Z = 4. Two different coordination geometries are present in 1: four-coordinate *pseudo*-tetrahedral with two monodentate nitrates, and five-coordinate distorted square-pyramidal with one bidentate nitrate occupying an axial and an equatorial position. In 2, only four-coordinate molecules are found; their structure is almost the same as the four-coordinate molecules in 1. These results indicate the near electronic energy equivalence of four and five-coordination about copper(II) in this compound. Furthermore, crystal 1 is a rare example of a pure compound which displays two different coordination numbers in the same crystal structure.

INTRODUCTION

We have been interested for some time in the role which *pseudo*-tetrahedral geometries might have in the coordination chemistry of copper(II).[1] Over the past

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two decades, several studies of transition metal complexes of the neutral alkaloid (-)-sparteine (Figure 1) have been reported.[2-9] The crystal and molecular structures of its complexes with Co(II),[3,9] Pd(II),[7] and Cu(II)[8] with various anions have been determined. It has long been recognized that the role of the anions in these complexes is important in the ultimate molecular structure, even when different monodentate anions were utilized. As a bidentate ligand, (-)-sparteine (SP) is also chiral (6R, 7S, 9S, 11S), and its structure is well understood.[10-11]

Copper(II) complexes which might model electron-transfer catalytic centers in metalloproteins are of special interest. Like the type I copper(II) *pseudo*-tetrahedral centers in metalloproteins, Cu(II)-sparteine complexes have low A_{11} values and positive reduction potentials. Our synthesis of the nitrate complex was prompted by our early interest[1] in Cu(II)-sparteine complexes as potential models for the *pseudo*-tetrahedral environment of type I copper(II) in metalloenzymes, and was an attempt to find that elusive set of conditions where the D_{2d} environment might be present *in solution*. The early data on Cu(SP)Cl$_2$ doped into Zn(SP)Cl$_2$ suggested a near *pseudo*-tetrahedral environment. This was confirmed later by Childers, *et al.*[8] but the low solubility of that compound precluded solution studies.

EXPERIMENTAL

Materials

All reagents and solvents were obtained commercially either from Fisher Scientific or Aldrich Chemicals and were used without further purification except where noted. Anhydrous ethanol was distilled from calcium hydride and stored under argon. The (-)-sparteine was purchased from Sigma Chemical Company. The anhydrous copper nitrate (Aldrich) was dried under vacuum at 60°C for 12 h before use.

Synthesis

The metal complex Cu(SP)(NO$_3$)$_2$ was prepared in a glove bag by mixing a triethylorthoformate/ethanol (1:5 by volume) solution of copper nitrate with a stoichiometric amount of (-)-sparteine in the same solvent mixture. The resulting blue precipitate was isolated by filtration, washed several times with cold absolute ethanol and dried under vacuum. The complex was purified by recrystallization from ethanol/dichloromethane (1:1 by volume) under carbon tetrachloride vapor.
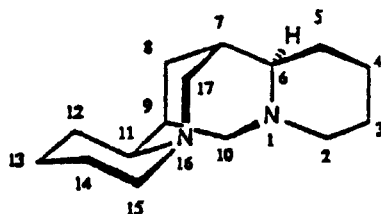

Figure 1   (-)-Sparteine. The symmetry of this neutral chiral alkaolid is 2 (C$_2$).

The resulting solid was collected and dried under vacuum over phosphorous pentoxide. *Anal.* Calcd for $C_{15}H_{26}N_4O_6Cu$: C, 42.7; H, 6.21; N, 13.28. Found: C, 42.6; H, 6.34; N, 13.32.

Physical Measurements

Electronic absorption spectra were measured on a Cary 17 spectrophotometer. Infrared spectra (4000–400 cm^{-1}) were obtained using KBr pellets with a Mattson Polaris FTIR spectrometer. Mass spectra were obtained on a JOEL JMS-DX 300 mass spectrometer in FAB mode. ESR spectra at 300 K and 100 K were obtained with a Varian E-9 spectrometer at approximately 9 GHz (X-Band) using variable temperature control to obtain data. The field was calibrated using DPPH as a g-value standard and a solution of VO^{+2} to calibrate the field. The molar conductance of a 10^{-3} M solution in ethanol at 300 K was measured with a CM-2A conductance meter (TOA Electronics).

Crystallography

Crystal data and experimental conditions are summarized in Table 1.

Crystal 1

Blue crystals suitable for X-ray analysis were grown at 25°C with some degree of difficulty by slow evaporation of a saturated acetonitrile solution. The crystals were thin platelets. Unit cell parameters were obtained by a least-squares refinement of

Table 1 Crystallographic data.

	Crystal 1	Crystal 2
Chemical formula	$CuC_{15}H_{26}N_4O_6$	$CuC_{15}H_{26}N_4O_6$
FW, AMU	421.94	421.94
Color	blue	blue
Crystal habit	platelet	prismatic
Crystal size (mm)	$0.15 \times 0.20 \times 0.45$	$0.30 \times 0.30 \times 0.40$
Crystal system	monoclinic	orthorhombic
Space group	$P2_1$	$P2_12_12_1$
T (K)	296	297
Radiation(Mo K_α)(Å)	0.71073	0.71073
Cell dimensions		
a(Å)	7.851(6)	7.863(4)
b(Å)	14.408(10)	12.410(4)
c(Å)	16.079(10)	18.050(6)
angles(°)	$\beta = 97.93(6)$	$\alpha = \beta = \gamma = 90$
Volume ($Å^3$)	1801(2)	1761(1)
Z	4	4
ρ(calc.)(g/cm^3)	1.556	1.591
μ(cm^{-1})	12.5	12.8
F(000) (e$^-$)	884	884
Residuals (%)		
R_1[a]	5.50	4.66
R_w[b]	4.86	6.33
Goodness of fit[c]	1.32	0.78

[a]$R_1 = \Sigma\|F_0| - |F_c\|/\Sigma|F_0|$. [b]$R_w = \{\Sigma w(\Delta F)^2/\Sigma wF_0^2\}^{0.5}$. [c]$GOF = \Sigma[w(\Delta F)^2/(N_0 - N_v)]^{0.5}$.

the setting angles of 18 reflections with $15°<2\theta<25°$. Axial photographs confirmed the monoclinic symmetry. A data set for the octants h,k,l and -h,k,l was collected on a Nicolet R3m/μ diffractometer using a graphite monochromator up to $2\theta \leq 55°$ by the ω-scan method at variable scan speeds, between 4 and 29° min^{-1}. Systematic absences and the presence of chiral (-)-sparteine molecules indicated that the space group of the crystal is $P2_1$. Two check reflections collected after every 48 reflections revealed no variation in intensity. Data were corrected for Lorentz and polarization effects. An absorption correction was not carried out.

All subsequent calculations were performed with the software package SHELXTL provided by Nicolet.[12] Of the 4715 reflections gathered, the 3033 unique reflections for which $I>2\sigma(I)$ were used in subsequent calculations. The copper atoms were located by Patterson methods. The remaining non-hydrogen atoms were found by difference Fourier methods. The structure was refined by blocked-cascade least-squares using SHELXTL. Non-hydrogen atoms were refined with anisotropic temperature factors, while all hydrogen atoms were placed in calculated positions 0.96Å from attached carbon nuclei and were not refined. A final difference Fourier revealed no missing or misplaced electron density.

Neutral atom scattering factors and anomalous scattering correction terms were taken from the International Tables for X-ray Crystallography.[13] The refined structures were plotted using the SHELXTL graphics package. Atomic coordinates and isotropic thermal parameters are given in Table 2. Selected bond distances and bond angles are given in Tables 3 and 4.

Crystal 2

Single crystals of $Cu(SP)(NO_3)_2$ were obtained by recrystallization at about 5°C from ethanol/dichloromethane (1:1 by volume) under carbon tetrachloride vapor. The resulting prismatic crystals were collected and dried *in vacuo* over phosphorous pentoxide. Preliminary crystallographic experiments and subsequent data collection were performed with an automated four-circle Nicolet P3 diffractometer equipped with a graphite monochromator and a pulse-height analyzer. Unit-cell dimensions were verified with axial photographs and refined by a least-squares fit of 35 reflections with $15°<2\theta<30°$. The orthorhombic space group $P2_12_12_1$ was assigned on the basis of the systematic absences. The θ-2θ scan mode was used to gather data in the +h, +k, +l octant with variable scan speeds (1.0 to 14.65° 2θ min^{-1}: most reflections were observed at slow scan speeds between 1.2° and 1.5° in 2θ min^{-1}. The intensities of three reflections were measured after every 97 reflections to monitor crystal stability. Only small random fluctuations of these check reflections were noted during the course of data collection. A φ scan of six reflections for which $10°<2\theta<60°$ and $83°<\chi<89°$ were used for an empirical absorption correction. The intensities measured were corrected for Lorentz and polarization effects. Of the 1784 unique reflections examined, only the 1568 for which $I > 3\sigma(I)$ were used for structure solution. The structure was solved by Patterson methods. All calculations were performed on a Micro-Vax II computer using the SHELXTL-PLUS program package. Several cycles of isotropic refinement of nonhydrogen atoms led to an R_1 value of 0.28. Further refinement including anisotropic thermal parameters for the nonhydrogen atoms reduced the R_1 value to 0.078. A difference Fourier synthesis showed the positions of 17 of the 26 hydrogen atoms. The positional parameters of the remaining nine hydrogen atoms were calculated. Attempts to refine the

Table 2 Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($\text{Å}^2 \times 10^3$).

	(a) Crystal 1			
	x	y	z	U*
Cu(1)	158(1)	1344	5722(1)	30(1)
N(1)	230(8)	396(5)	6654(4)	30(3)
N(2)	−2230(9)	986(5)	5285(4)	34(3)
C(1)	1990(11)	485(6)	7159(5)	35(3)
C(2)	2449(12)	−298(7)	7774(5)	39(3)
C(3)	2351(13)	−1225(7)	7331(6)	53(4)
C(4)	557(12)	−1333(7)	6858(6)	50(4)
C(5)	48(12)	−542(7)	6247(6)	42(4)
C(6)	−1782(12)	−678(7)	5782(6)	46(4)
C(7)	−1156(10)	594(7)	7161(5)	35(3)
C(8)	−3069(13)	−561(8)	6371(7)	57(4)
C(9)	−2929(11)	441(7)	6680(6)	39(3)
C(10)	−2190(13)	−30(7)	5033(6)	49(4)
C(11)	−3401(11)	1094(7)	5950(6)	41(4)
C(12)	−3496(12)	2123(7)	6183(6)	46(4)
C(13)	−4113(12)	2712(8)	5421(6)	53(4)
C(14)	−3097(11)	2549(7)	4718(6)	48(4)
C(15)	−2975(11)	1511(8)	4522(5)	45(4)
N(3)	1930(9)	1289(8)	4439(4)	49(3)
O(1)	747(8)	1790(5)	4607(4)	54(3)
O(2)	2688(8)	1430(8)	3845(4)	85(3)
O(3)	2316(9)	591(6)	4913(5)	61(3)
N(4)	1741(10)	2963(6)	6313(5)	40(3)
O(4)	2152(8)	2096(5)	6262(4)	50(3)
O(5)	2848(8)	3502(5)	6561(4)	51(3)
O(6)	229(8)	3171(6)	6096(5)	70(3)
Cu(2)	9426(1)	3660(1)	9317(1)	32(1)
N(1A)	6956(8)	3786(5)	9498(4)	34(3)
N(2A)	9099(8)	4585(5)	8399(4)	27(2)
C(1A)	6502(13)	3181(8)	10199(6)	55(4)
C(2A)	6312(13)	2154(8)	9960(7)	58(4)
C(3A)	5056(14)	2022(8)	9173(7)	67(5)
C(4A)	5605(12)	2644(7)	8480(7)	50(4)
C(5A)	5662(11)	3643(8)	8739(6)	44(3)
C(6A)	5919(11)	4342(7)	8058(6)	44(4)
C(7A)	6873(11)	4781(7)	9777(6)	39(4)
C(8A)	5590(11)	5323(7)	8393(6)	43(4)
C(9A)	7028(11)	5484(7)	9104(6)	43(4)
C(10A)	7634(11)	4304(7)	7768(5)	37(3)
C(11A)	8768(11)	5500(6)	8787(5)	30(3)
C(12A)	9011(11)	6330(8)	8225(6)	49(3)
C(13A)	10716(13)	6294(8)	7875(6)	61(4)
C(14A)	10919(14)	5395(7)	7437(6)	48(4)
C(15A)	10718(11)	4596(6)	8017(5)	34(3)
N(3A)	10380(10)	1976(5)	9076(5)	71(3)
O(1A)	10112(9)	2379(4)	9767(4)	48(3)
O(2A)	10777(10)	1165(4)	9072(5)	67(3)
O(3A)	10264(9)	2483(4)	8429(4)	55(3)
N(4A)	11821(11)	4182(6)	10646(5)	46(3)
O(4A)	11774(8)	4163(5)	9845(4)	47(3)
O(5A)	10524(9)	3944(5)	10927(4)	58(3)
O(6A)	13114(10)	4424(8)	11078(5)	96(4)

Table 2 *Continued*

	(b) Crystal 2			
	x	*y*	*z*	U^a
Cu(1)	9201.6(10)	1089.8(6)	1806.6(4)	32.2(2)
O(1)	10142(8)	2540(4)	2135(3)	52(2)
O(2)	12231(7)	3556(4)	1753(2)	59(2)
O(3)	11519(8)	2111(4)	1134(3)	53(2)
O(4)	10895(7)	406(4)	2459(3)	49(2)
O(5)	11462(12)	120(7)	3611(3)	50(2)
O(6)	9087(8)	935(5)	3271(3)	63(2)
N(1)	9008(8)	− 200(4)	1100(3)	31(2)
N(2)	7033(7)	1692(5)	1407(3)	36(2)
N(3)	11333(8)	2751(5)	1667(3)	40(2)
N(4)	10491(8)	515(5)	3145(3)	38(2)
C(1)	10544(10)	− 904(6)	1242(4)	45(2)
C(2)	10802(14)	− 1783(7)	671(4)	57(3)
C(3)	11008(15)	− 1269(8)	− 96(4)	66(3)
C(4)	9460(15)	− 613(7)	− 263(4)	62(3)
C(5)	9105(12)	254(6)	324(3)	40(2)
C(6)	7469(12)	867(7)	138(4)	52(2)
C(7)	7387(11)	− 788(5)	1265(4)	43(2)
C(8)	5912(14)	180(8)	248(5)	59(3)
C(9)	5826(12)	− 132(7)	1066(4)	49(2)
C(10)	7247(12)	1915(4)	606(4)	50(2)
C(11)	5570(9)	902(6)	1528(4)	43(2)
C(12)	5356(11)	705(7)	2359(5)	46(2)
C(13)	4933(12)	1750(7)	2755(5)	55(3)
C(14)	6257(13)	2609(6)	2585(5)	54(3)
C(15)	6540(10)	2744(5)	1771(5)	46(2)

^{a}The equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

calculated hydrogen positional and thermal parameters led to erratic behavior, so these were held fixed at their calculated positions. The error indices converged at $R_1 = 0.057$ and $R_w = 0.076$. The absolute configuration was determined by refinement of the inverse structure: its final error indices are $R_1 = 0.046$ and $R_w = 0.063$. A final difference Fourier showed residual electron density of height 1.0 $e\text{Å}^{-3}$ 1.0Å from the Cu atom. The final structure is the result of full-matrix least squares refinement using all 1784 reflections: for this $R_1 = 0.054$ and $R_2 = 0.070$. Selected bond distances and angles are given in Tables 3 and 4.

DISCUSSION

There has been considerable interest in recent years in the coordination chemistry and stereo-electronic properties of copper(II) compounds which mimic aspects of the properties of copper in proteins. Of special interest has been type I copper(II), the unique "blue" sites which are often referenced as *pseudo*-tetrahedral geometries. Solomon *et al.* recently provided a thorough review of these systems.[14] Our efforts in looking at copper(II) complexes of sparteine have concentrated on models for these sites. The observation of both four- and five-coordinate geometry in the solid state was a surprise, even though the frozen-glass electron-spin-resonance spectrum had suggested that two different copper(II) species were present in solution. Perhaps

Table 3 Selected bond lengths (Å).

(a) Crystal 1			
Cu(1)–N(1)	2.023(7)	Cu(1)-N(2)	1.978(7)
Cu(1)-O(1)	2.018(7)	Cu(1)-O(4)	2.002(7)
N(1)-C(1)	1.509(10)	N(1)-C(5)	1.500(12)
N(1)-C(7)	1.475(11)	N(2)-C(10)	1.520(13)
N(2)-C(11)	1.511(12)	N(2)-C(15)	1.490(11)
C(1)-C(2)	1.512(13)	C(2)-C(3)	1.511(13)
C(3)-C(4)	1.513(13)	C(4)-C(5)	1.521(14)
C(5)-C(6)	1.538(13)	C(6)-C(8)	1.487(15)
C(6)-C(10)	1.523(14)	C(7)-C(9)	1.512(11)
C(8)-C(9)	1.526(15)	C(9)-C(11)	1.509(13)
C(11)-C(12)	1.534(14)	C(12)-C(13)	1.514(14)
C(13)-C(14)	1.490(14)	C(14)-C(15)	1.534(15)
N(3)-O(1)	1.234(12)	N(3)-O(2)	1.210(10)
N(3)-O(3)	1.272(13)	N(4)-O(4)	1.295(11)
N(4)-O(5)	1.192(10)	N(4)-O(6)	1.227(10)
Cu(2)-N(1A)	2.007(7)	Cu(2)-N(2A)	1.979(7)
Cu(2)-O(1A)	2.028(7)	Cu(2)-O(3A)	2.369(7)
Cu(2)-O(4A)	2.052(6)	N(1A)-C(1A)	1.506(13)
N(1A)-C(5A)	1.491(10)	N(1A)-C(7A)	1.506(13)
N(2A)-C(10A)	1.482(10)	N(2A)-C(11A)	1.496(11)
N(2A)-C(15A)	1.487(11)	C(1A)-C(2A)	1.531(16)
C(2A)-C(3A)	1.505(14)	C(3A)-C(4A)	1.538(16)
C(4A)-C(5A)	1.498(15)	C(5A)-C(6A)	1.520(14)
C(6A)-C(8A)	1.547(14)	C(6A)-C(10A)	1.486(13)
C(7A)-C(9A)	1.500(14)	C(8A)-C(9A)	1.509(12)
C(9A)-C(11A)	1.522(13)	C(11A)-C(12A)	1.527(14)
C(12A)-C(13A)	1.522(14)	C(13A)-C(14A)	1.493(15)
C(14A)-C(15A)	1.503(13)	N(3A)-O(1A)	1.297(10)
N(3A)-O(2A)	1.209(10)	N(3A)-O(3A)	1.263(10)
N(4A)-O(4A)	1.284(11)	N(4A)-O(5A)	1.218(12)
N(4A)-O(6A)	1.200(11)		
(b) Crystal 2			
Cu(1)-N(1)	2.052(5)	Cu(1)-N(2)	1.997(6)
Cu(1)-O(1)	2.033(6)	Cu(1)-O(4)	1.970(5)
Cu(1)-O(3)	2.530(6)	Cu(1)-O(6)	2.653(6)
N(1)-C(1)	1.512(10)	N(1)-C(5)	1.512(7)
N(1)-C(7)	1.499(10)	N(2)-C(10)	1.481(9)
N(2)-C(11)	1.528(9)	N(2)-C(15)	1.513(9)
C(1)-C(2)	1.514(11)	C(2)-C(3)	1.532(11)
C(3)-C(4)	1.495(15)	C(4)-C(5)	1.535(10)
C(5)-C(6)	1.532(12)	C(6)-C(8)	1.505(14)
C(6)-C(10)	1.561(11)	C(7)-C(9)	1.517(12)
C(8)-C(9)	1.528(11)	C(9)-C(11)	1.543(11)
C(11)-C(12)	1.531(11)	C(12)-C(13)	1.515(12)
C(13)-C(14)	1.521(13)	C(14)-C(15)	1.496(13)
N(3)-O(1)	1.287(8)	N(4)-O(4)	1.285(8)
N(3)-O(2)	1.232(8)	N(4)-O(5)	1.202(10)
N(3)-O(3)	1.257(8)	N(4)-O(6)	1.241(9)

most exciting, however, is that *some* type I copper(II) sites are now thought to be "pseudo" five-coordinate. The structures of several azurins show that an *additional* carbonyl oxygen of the protein backbone occupies a site *trans* to the thioether (axial) coordination site at a distance of 3.1Å.[15,16] Yet, the two types of sites apparently

Table 4 Selected bond angles (°).

(a) Crystal 1			
N(1)-Cu(1)-N(2)	90.9(3)	N(1)-Cu(1)-O(1)	152.5(3)
N(2)-Cu(1)-O(1)	95.1(3)	N(1)-Cu(1)-O(4)	96.0(3)
N(2)-Cu(1)-O(4)	160.4(3)	O(1)-Cu(1)-O(4)	87.2(3)
Cu(1)-N(1)-C(1)	105.7(5)	Cu(1)-N(1)-C(5)	107.1(5)
C(1)-N(1)-C(5)	109.7(7)	Cu(1)-N(1)-C(7)	109.3(5)
C(1)-N(1)-C(7)	112.2(6)	C(5)-N(1)-C(7)	112.5(7)
Cu(1)-N(2)-C(10)	107.0(5)	Cu(1)-N(2)-C(11)	111.1(5)
C(10)-N(2)-C(11)	108.9(7)	Cu(1)-N(2)-C(15)	113.9(6)
C(10)-N(2)-C(15)	106.9(7)	C(11)-N(2)-C(15)	108.8(7)
N(1)-C(1)-C(2)	114.0(7)	C(1)-C(2)-C(3)	111.1(7)
C(2)-C(3)-C(4)	108.1(8)	C(3)-C(4)-C(5)	113.1(8)
N(1)-C(5)-C(4)	113.1(7)	N(1)-C(5)-C(6)	110.7(8)
C(4)-C(5)-C(6)	111.3(8)	C(5)-C(6)-C(8)	110.4(8)
C(5)-C(6)-C(10)	112.7(8)	C(8)-C(6)-C(10)	110.4(8)
N(1)-C(7)-C(9)	112.8(7)	C(6)-C(8)-C(9)	106.8(8)
C(7)-C(9)-C(8)	108.9(8)	C(7)-C(9)-C(11)	114.6(8)
C(8)-C(9)-C(11)	109.8(8)	N(2)-C(10)-C(6)	112.9(8)
N(2)-C(11)-C(9)	112.2(7)	N(2)-C(11)-C(12)	109.1(8)
C(9)-C(11)-C(12)	115.3(8)	C(11)-C(12)-C(13)	111.4(8)
C(12)-C(13)-C(14)	112.4(8)	C(13)-C(14)-C(15)	111.4(8)
N(2)-C(15)-C(14)	110.8(7)	O(1)-N(3)-O(2)	122.8(10)
O(1)-N(3)-O(3)	117.1(8)	O(2)-N(3)-O(3)	120.1(10)
Cu(1)-O(1)-N(3)	106.2(6)	O(4)-N(4)-O(5)	118.2(7)
O(4)-N(4)-O(6)	117.2(8)	O(5)-N(4)-O(6)	124.7(9)
Cu(1)-O(4)-N(4)	111.3(5)	N(1A)-Cu(2)-N(2A)	91.1(3)
N(1A)-Cu(2)-O(1A)	104.2(3)	N(2A)-Cu(2)-O(1A)	151.6(3)
N(1A)-Cu(2)-O(3A)	120.4(3)	N(2A)-Cu(2)-O(3A)	92.9(3)
O(1A)-Cu(2)-O(3A)	58.7(2)	N(1A)-Cu(2)-O(4A)	137.6(3)
N(2A)-Cu(2)-O(4A)	95.0(3)	O(1A)-Cu(2)-O(4A)	89.7(3)
O(3A)-Cu(2)-O(4A)	101.2(3)	Cu(2)-N(1A)-C(1A)	112.9(5)
Cu(2)-N(1A)-C(5A)	115.6(5)	C(1A)-N(1A)-C(5A)	109.1(7)
Cu(2)-N(1A)-C(7A)	102.2(5)	C(1A)-N(1A)-C(7A)	107.6(7)
C(5A)-N(1A)-C(7A)	108.8(7)	Cu(2)-N(2A)-C(10A)	109.6(5)
Cu(2)-N(2A)-C(11A)	107.1(5)	C(10A)-N(2A)-C(11A)	111.3(6)
Cu(2)-N(2A)-C(15A)	106.6(5)	C(10A)-N(2A)-C(15A)	110.3(6)
C(11A)-N(2A)-C(15A)	111.8(6)	N(1A)-C(1A)-C(2A)	113.4(8)
C(1A)-C(2A)-C(3A)	111.3(9)	C(2A)-C(3A)-C(4A)	108.6(9)
C(3A)-C(4A)-C(5A)	111.1(9)	N(1A)-C(5A)-C(4A)	110.5(8)
N(1A)-C(5A)-C(6A)	110.8(8)	C(4A)-C(5A)-C(6A)	116.0(8)
C(5A)-C(6A)-C(8A)	108.0(8)	C(5A)-C(6A)-C(10A)	114.7(8)
C(8A)-C(6A)-C(10A)	110.2(8)	N(1A)-C(7A)-C(9A)	114.6(8)
C(6A)-C(8A)-C(9A)	105.1(7)	C(7A)-C(9A)-C(8A)	108.4(8)
C(7A)-C(9A)-C(11A)	114.7(7)	C(8A)-C(9A)-C(11A)	111.2(8)
N(2A)-C(10A)-C(6A)	115.2(7)	N(2A)-C(11A)-C(9A)	110.0(7)
N(2A)-C(11A)-C(12A)	113.6(7)	C(9A)-C(11A)-C(12A)	113.7(7)
C(11A)-C(12A)-C(13A)	112.3(8)	C(12A)-C(13A)-C(14A)	111.1(9)
C(13A)-C(14A)-C(15A)	110.1(8)	N(2A)-C(15A)-C(14A)	115.7(7)
O(1A)-N(3A)-O(2A)	120.6(8)	O(1A)-N(3A)-O(3A)	116.4(7)
O(2A)-N(3A)-O(3A)	123.0(8)	Cu(2)-O(1A)-N(3A)	99.7(5)
Cu(2)-O(3A)-N(3A)	85.0(5)	O(4A)-N(4A)-O(5A)	117.1(8)
O(4A)-N(4A)-O(6A)	119.4(9)	O(5A)-N(4A)-O(6A)	123.4(9)
Cu(2)-O(4A)-N(4A)	108.8(6)		

Table 4 *Continued*

(b) Crystal			
N(1)-Cu(1)-N(2)	90.2(2)	N(1)-Cu(1)-O(1)	153.9(2)
N(2)-Cu(1)-O(1)	94.2(2)	N(1)-Cu(1)-O(4)	94.9(2)
N(2)-Cu(1)-O(4)	162.7(2)	O(1)-Cu(1)-O(4)	87.8(2)
N(1)-Cu(1)-O(6)	124.1(2)	O(1)-Cu(1)-O(3)	55.8(2)
O(4)-Cu(1)-O(6)	52.8(2)	O(3)-Cu(1)-O(4)	90.9(2)
N(1)-Cu(1)-O(6)	124.1(2)	N(2)-Cu(1)-O(3)	104.7(2)
C(1)-N(1)-C(5)	106.4(4)	Cu(1)-N(1)-C(7)	108.6(4)
C(1)-N(1)-C(7)	111.3(5)	C(5)-N(1)-C(7)	114.1(6)
Cu(1)-N(2)-C(10)	109.0(5)	Cu(1)-N(2)-C(11)	110.5(4)
C(10)-N(2)-C(11)	110.2(5)	Cu(1)-N(2)-C(15)	112.6(4)
C(10)-N(2)-C(15)	107.0(5)	C(11)-N(2)-C(15)	107.4(5)
N(1)-C(1)-C(2)	114.1(6)	C(1)-C(2)-C(3)	109.2(7)
C(2)-C(3)-C(4)	108.9(8)	C(3)-C(4)-C(5)	113.0(7)
N(1)-C(5)-C(4)	112.8(6)	N(1)-C(5)-C(6)	110.3(6)
C(1)-C(5)-C(6)	110.4(6)	C(5)-C(6)-C(8)	111.9(7)
C(5)-C(6)-C(10)	112.9(6)	C(8)-C(6)-C(10)	108.0(7)
N(1)-C(7)-C(9)	112.3(6)	C(6)-C(8)-C(9)	107.9(7)
C(7)-C(9)-C(8)	109.3(7)	C(7)-C(9)-C(11)	115.0(7)
C(8)-C(9)-C(11)	108.6(7)	N(2)-C(10)-C(6)	112.7(6)
N(2)-C(11)-C(9)	111.0(6)	N(2)-C(11)-C(12)	109.5(6)
C(9)-C(11)-C(12)	114.4(6)	C(11)-C(12)-C(13)	110.5(7)
C(12)-C(13)-C(14)	111.2(7)	C(13)-C(14)-C(15)	111.2(7)
N(2)-C(15)-C(14)	111.6(6)	O(4)-N(4)-O(5)	118.9(7)
O(1)-N(3)-O(2)	120.0(6)	O(4)-N(4)-O(6)	116.2(6)
O(1)-N(3)-O(3)	117.2(6)	O(5)-N(4)-O(6)	125.0(7)
O(2)-N(3)-O(3)	122.8(6)	Cu(1)-O(4)-N(4)	111.3(4)
Cu(1)-O(1)-N(3)	104.7(4)		

carry out a similar function. This is not necessarily surprising since it has long been known that the copper(II) site in stellacyanin, also labeled a type I copper site, must be different because no methionine residue exists in its sequence.[17]

The solution molar conductivity of $Cu(SP)(NO_3)_2$ in ethanol was 16.0 Ω cm^{-2} mol^{-1}. This is similar to other molecular species and indicates that the compound does not dissociate in this solvent. We found the molar conductivity of $Cu(SP)Cl_2$ to be 13.5 Ω cm^{-2} mol^{-1} and $[SPH_2][CuCl_4]$ to be 102.4 Ω cm^{-2} mol^{-1} in the same solvent.

Atomic coordinates for both crystals are given in Table 2. Selected bond distances and angles are presented in Tables 3 and 4. Figures 2, 3 and 4 show the three separate molecules whose structures have been determined. The unique situation of nitrate being sometimes monodentate and sometimes bidentate, found in **1**, has apparently not been observed before. One could imagine a four- and five-coordinate complex present in the same crystal, but to have both with the same stoichiometry seems truly unusual. The geometry of the four-coordinate complex is twisted planar where the four bond angles, in what might be imagined as the plane, are all near 90°. The twist angle between the N(2)-Cu-N(1) and the O(1)-Cu-O(4) plane is 34.2° for **1** and 31.7° for **2**, where a 90° twist angle would result in a C_{2v} inner coordination shell geometry. The geometry of the five-coordinate complex is more difficult to describe. The N(1A), N(2A), O(1A) and O(4A) ligating atoms can be imagined as the basal plane of the square-pyramidal structure with the O(3A) atom occupying the axial position. The N(1A)-Cu-N(2A) plane is twisted by 51.1° from the O(1A)-Cu-O(4A) plane. The
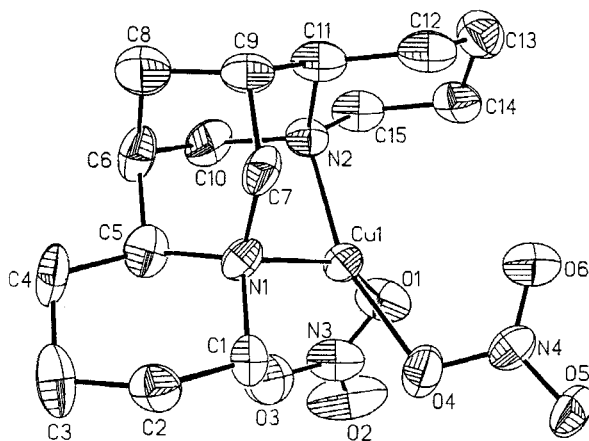
Figure 2   The four-coordinate Cu(SP)(NO₃)₂ Molecule in crystal 1. Ellipsoids of 50% probability are used.

Cu(3A) bond distance of 2.369(7)Å is, however, significantly longer than either of the other two Cu-O bond distances as might be expected for the "axial" bond distance. The Cu-O(5A) distance of 2.644 Å does not appear to constitute a Cu-O bond.

Features of the optical absorption spectra and infrared spectra are given in Table 5. The two low-energy optical bands likely correspond to $d_{x^2-y^3} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{z^2}$ ligand field transitions as has been suggested eariler.[1] The electron spin-resonance spectrum of Cu(SP)(NO₃)₂ in a toluene/CHCl₃ (1:1) frozen solution displayed a very

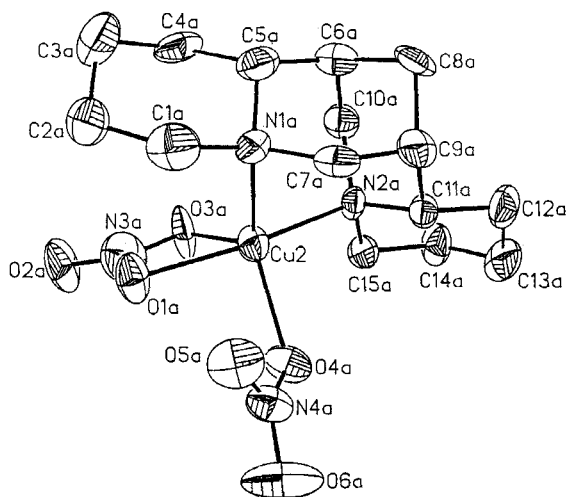**Figure 3**   The five-coordinate Cu(SP)(NO₃)₂ molecule in crystal 1. Ellipsoids of 50% probability are used.

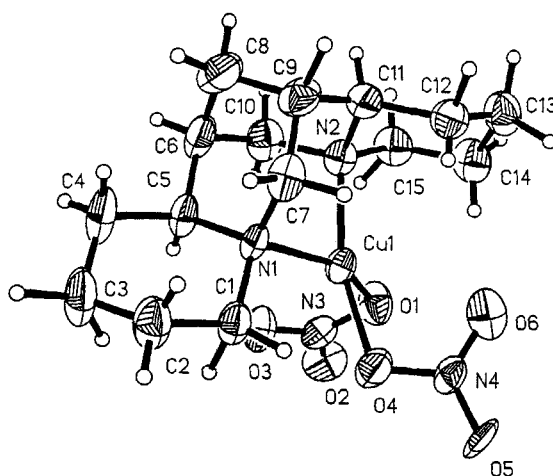**Figure 4** The four-coordinate Cu(SP)(NO₃)₂) molecule in crystal 2 is shown in an orientation to permit comparison with the corresponding molecule in crystal 1 (shown in Figure 2). Elipsoids of 50% probability are used.

small A_{11} value of 118G. While there was some asymmetry in the line shapes present, it would appear that in this solvent system (non-coordinating), the predominant species is the four coordinate *pseudo*-tetrahedral complex. The A_{11} value for Cu(SP)Cl₂ in a Zn(SP)Cl₂ matrix was 90.4(5) G, and that for Cu(SP)Br₂ in a Zn(SP)Br₂ matrix was estimated to be 124 G.[1] The value for Cu(SP)(NO₃)₂ in a frozen solution is in this range and suggests a *pseudo*-tetrahedral geometry in solution.

SUPPLEMENTARY DATA

Tables of (1) H-atom coordinates and isotropic thermal parameters, (2) anisotropic thermal parameters for non-hydrogen atoms, and (3) observed and calculated structure factors with estimated standard deviations are available from RDB

Table 5 Optical and infrared features of Cu(SP)(NO₃)₂.

Optical (nm,ε)[a]		IR(cm⁻¹)
320 (5245)[b]		2940 (s)
698 (278)		2850(m)
970 (180, broad)	($\sqrt{5}$ NO₃)	1485 (vs)
	($\sqrt{3}$ NO₃)	1385 (vs)
	($\sqrt{1}$ NO₃)	1293 (vs)
	($\sqrt{2}$ NO₃)	1012 (s)

[a] Solvent CH₂Cl₂
[b] Molar absorptivity (L mol⁻¹ cm⁻¹)

Acknowledgement

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