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X-Ray Crystallographic Analysis of Bis[2-(n-propylmercaptomethyl)pyridine]-copper(II) Diperchlorate, and Spectroscopic and Redox Properties of Its Related $Cu^{II}N_2S_2$ Complexes

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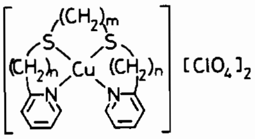
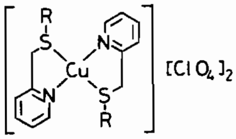
A single-crystal X-ray structure analysis of the title copper(II) complex reveals a structure in which the copper atom is centrosymmetrically coordinated by two pyridyl nitrogen atoms [Cu–N, 2.015(3) Å], two thioether sulfur atoms [Cu–S, 2.366(1) Å], and two oxygen atoms of perchlorate ions [Cu–O, 2.501(3) Å]. The triclinic crystal, space group $P\bar{1}$, *has cell dimensions* $a = 8.955(1)$, $b = 8.794(1)$, $c = 8.517(1)$ Å, $\alpha = 104.37(1)$, $\beta = 109.723(8)$, $\gamma = 78.86(1)°$, *and* $Z = 1$. *Block-diagonal least-squares refinement, based on 2444 independent reflections with* $|F_o| > 3\sigma(F)$, *yields an R factor of 0.044. Electronic absorption and electron spin resonance spectra, as well as redox potentials* ($E^{0'}$) *of the* Cu^{II}-N_2S_2 *complexes containing thioether-sulfur and pyridyl-, amino-, or imidazolyl-nitrogen donor atoms, were examined. Both the plots of the wave number of d–d band maxima vs.* $E^{0'}$ *and of* $^{63/65}Cu$*-hyperfine coupling constants* $|A_\parallel|$ *vs.* $g_\parallel$ *exhibited a linear relationship, indicating that π-acceptor property of nitrogen-containing ligands contributes mainly to the properties of these* $Cu^{II}N_2S_2$ *complexes.*

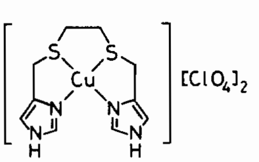
Introduction

Previously we reported the X-ray structure of bis-[4-(n-propylmercaptomethyl)imidazole]copper(II) diperchlorate and kinetics of the oxidation–reduction reactions of this complex and its analogs with ferrocene [1]. In order to obtain a better understanding of the properties of the $Cu^{II}N_2S_2$ type complexes, which are analogous to active sites of blue (type I) copper proteins [2, 3], we have undertaken a study of the spectroscopic and electrochemical properties of various copper(II) complexes with N_2S_2 ligands. This paper describes the X-ray structure of bis[2-(n-propylmercaptomethyl)pyridine]copper(II) diperchlorate (*6*), together with the spectroscopic and electrochemical properties of this complex and its analogs with the $Cu^{II}N_2S_2$ skeleton (*1*–*5* and *7*–*13*).





m = 2, n = 1 (*1*)
m = 3, n = 1 (*2*)
m = 3, n = 2 (*3*)
R = Me (*4*), Et (*5*), Pr^n (*6*), $PhCH_2$ (*7*) and Bu^t (*8*)



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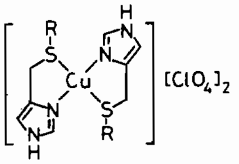

R = Pr^n (*10*), $PhCH_2$ (*11*), Bu^t (*12*)

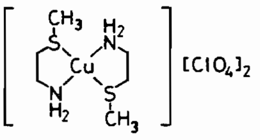

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TABLE I. Atomic Coordinates (×10^4; H, ×10^3) and Thermal Parameters (×10^4; H, ×10^3) for $[Cu(Pr^nSCH_2py)_2][ClO_4]_2$ (*6*) with the Standard Deviations in Parentheses.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0(0)	0(0)	0(0)	303(2)	400(3)	298(2)	−115(2)	105(2)	16(2)
Cl	2670.5(9)	−2385(1)	3295(1)	454(4)	543(4)	398(4)	−76(3)	104(3)	87(3)
S	493.5(9)	2040.7(9)	2450.9(9)	401(4)	452(4)	335(3)	−129(3)	123(3)	10(3)
O(1)	2150(3)	−1660(3)	1816(4)	710(18)	748(18)	575(16)	−5(14)	95(13)	273(14)
O(2)	4117(4)	−1808(5)	4352(5)	702(21)	1420(34)	842(24)	−306(21)	−243(18)	45(23)
O(3)	2954(5)	−4036(4)	2749(5)	1443(34)	542(18)	1049(28)	−46(19)	304(25)	213(18)
O(4)	1493(5)	−1962(6)	4123(6)	1048(30)	1978(46)	1134(32)	172(29)	743(27)	529(32)
N	1794(3)	756(3)	−415(3)	307(11)	406(12)	332(12)	−74(9)	98(9)	81(10)
C(1)	2015(4)	447(4)	−1964(4)	404(15)	508(17)	392(16)	−80(13)	156(13)	96(13)
C(2)	3247(4)	972(4)	−2231(5)	542(19)	572(20)	557(20)	−76(15)	304(16)	138(16)
C(3)	4285(4)	1846(4)	−887(5)	471(18)	609(21)	705(24)	−142(16)	307(17)	108(18)
C(4)	4059(4)	2194(4)	685(5)	335(15)	510(18)	628(21)	−147(13)	133(14)	75(15)
C(5)	2808(3)	1629(3)	894(4)	297(13)	397(14)	390(15)	−61(11)	80(11)	69(12)
C(6)	2562(4)	1966(4)	2607(4)	357(15)	538(18)	381(15)	−135(13)	44(12)	42(13)
C(7)	−356(4)	3856(4)	1650(5)	569(20)	475(18)	534(20)	−81(15)	167(16)	47(15)
C(8)	−2110(5)	4267(6)	1644(6)	648(25)	838(29)	644(26)	91(22)	128(20)	16(22)
C(9)	−2309(6)	4967(6)	3357(6)	826(32)	927(34)	778(31)	109(26)	339(26)	135(26)
HC(1)	130(4)	−14(4)	−296(4)	20(9)					
HC(2)	339(5)	70(5)	−323(6)	50(13)					
HC(3)	510(5)	227(5)	−101(5)	39(11)					
HC(4)	472(5)	286(4)	172(5)	34(11)					
HC(61)	316(4)	115(4)	316(5)	29(10)					
HC(62)	286(4)	301(4)	328(4)	14(8)					
HC(71)	−19(5)	371(5)	60(5)	38(11)					
HC(72)	30(4)	457(4)	237(5)	32(10)					
HC(81)	−277(6)	317(6)	104(6)	69(15)					
HC(82)	−272(9)	535(8)	137(9)	138(27)					
HC(91)	−190(6)	406(6)	396(7)	85(18)					
HC(92)	−164(6)	581(6)	363(7)	88(18)					
HC(93)	−395(6)	527(6)	292(7)	85(18)					

Experimental

Preparations of the Copper(II) Complexes (1–13)

1,6-Bis(2-pyridyl)-2,5-dithiahexanecopper(II) (*1*), 1,7-bis(2-pyridyl)-2,6-dithiaheptanecopper(II) (*2*), and 1,8-bis(2-pyridyl)-3,6-dithiaoctanecopper(II) diperchlorate (*3*) were prepared by literature methods [4, 5].

2-(Alkylmercaptomethyl)pyridine, $RSCH_2py$, (R = Me, Et, Pr^n, $PhCH_2$, and Bu^t) were prepared according to the literature [6]. To an ethanol (10 cm^3) solution of $MeSCH_2py$ (0.5 g, 3.6 mmol) was added $Cu(ClO_4)_2 \cdot 6H_2O$ (0.67 g, 1.8 mmol) dissolved in the same solvent (10 cm^3) and the solution was stirred for 30 min at room temperature. Green microcrystals of $[Cu(MeSCH_2py)_2][ClO_4]_2$ (*4*) obtained were collected by filtration, washed with diethyl ether, and dried *in vacuo*. Other, S,S′-dialkyl analogs, $[Cu(RSCH_2py)_2][ClO_4]_2$ (R = Et (*5*), Pr^n (*6*), $PhCH_2$ (*7*), Bu^t (*8*)), were prepared similarly. *Anal.* Calcd. (%) for $[Cu(RSCH_2py)_2][ClO_4]_2$ in parentheses. *4*: C, 31.18 (31.09); H, 3.49 (3.35); N, 5.18 (5.18). *5*: C, 33.73 (33.78); H, 4.08 (3.90); N, 4.95 (4.92). *6*: C, 36.49 (36.21); H, 4.57 (4.39); N, 5.01 (4.69). *7*: C, 44.98 (45.06); H, 3.93 (3.78); N, 4.32 (4.04). *8*: C, 38.11 (38.43); H, 5.08 (4.84); N, 4.72 (4.48).

1,6-Bis(4-imidazolyl)-2,5-dithiahexanecopper(II) diperchlorate (*9*) and bis[4-(alkylmercaptomethyl)-imidazole]copper(II) diperchlorates, $[Cu(RSCH_2\text{-}im)_2][ClO_4]_2$ (R = Pr^n (*10*), $PhCH_2$ (*11*), and Bu^t (*12*)), were prepared by the methods described previously [1]. Bis-(β-methylmercaptoethylamine)-copper(II) diperchlorate (*13*) was also prepared according to the literature [7].

Physical Measurements

Electronic absorption, electron spin resonance spectra and cyclic voltammograms were measured as described previously [1].

X-Ray Crystal Structure Determination

A suitable single crystal of *6* with approximate dimensions 0.11 × 0.27 × 0.30 mm was mount-

TABLE II. Selected Bond Distances and Angles for $[Cu(Pr^nSCH_2py)_2][ClO_4]_2$ (*6*) with the Standard Deviations in Parentheses.

Bond Distances (Å)

Cu–S	2.366(1)	C(3)–C(4)	1.373(6)
Cu–O(1)	2.501(3)	C(4)–C(5)	1.388(5)
Cu–N	2.015(3)	C(5)–C(6)	1.497(5)
S–C(6)	1.802(3)	C(7)–C(8)	1.541(6)
S–C(7)	1.820(4)	C(8)–C(9)	1.492(7)
N–C(1)	1.352(4)	Cl–O(1)	1.449(3)
N–C(5)	1.348(3)	Cl–O(2)	1.409(4)
C(1)–C(2)	1.379(6)	Cl–O(3)	1.411(3)
C(2)–C(3)	1.373(5)	Cl–O(4)	1.403(5)

Bond Angles (°)

S–Cu–O(1)	85.3(1)	Cu–N–C(1)	122.8(2)
S–Cu–N	83.8(1)	Cu–N–C(5)	119.0(2)
O(1)–Cu–N	85.7(1)	C(1)–N–C(5)	118.2(3)
O(1)–Cl–O(2)	106.9(2)	N–C(1)–C(2)	122.2(3)
O(1)–Cl–O(3)	108.3(2)	C(1)–C(2)–C(3)	119.2(4)
O(1)–Cl–O(4)	108.8(2)	C(2)–C(3)–C(4)	119.2(4)
O(2)–Cl–O(3)	109.2(2)	C(3)–C(4)–C(5)	119.4(3)
O(2)–Cl–O(4)	111.1(2)	N–C(5)–C(4)	121.7(3)
O(3)–Cl–O(4)	112.3(3)	N–C(5)–C(6)	118.1(3)
Cu–S–C(6)	93.6(1)	C(4)–C(5)–C(6)	120.2(3)
Cu–S–C(7)	104.7(1)	S–C(6)–C(5)	112.0(2)
C(6)–S–C(7)	101.2(2)	S–C(7)–C(8)	109.6(3)
Cu–O(1)–Cl	147.2(2)	C(7)–C(8)–C(9)	114.1(3)

ed on a fiber. The space group and initial cell dimensions were determined from oscillation and Weissenberg photographs. Accurate cell constants were determined by the least-squares refinement of angular setting of 48 independent reflections with 2θ values (29–38°).

Crystal Data

$C_{18}H_{26}Cl_2CuN_2O_8S_2$, $M = 597.0$, Triclinic, space group $P\bar{1}$, $a = 8.955(1)$, $b = 8.794(1)$, $c = 8.517(1)$ Å, $\alpha = 104.37(1)$, $\beta = 109.723(8)$, $\gamma = 78.86(1)°$, $U = 607.1(1)$ Å^3, $Z = 1$, $D_c = 1.633(1)$ g cm^{-3}, $F(000) = 307$, μ(Mo-Kα) = 13.7 cm^{-1}.

2482 Intensities were measured up to $2\theta_{max}$ of 55° using graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and the ω–2θ scan technique on an automated Rigaku four-circle diffractometer. Lorentz and polarization corrections were applied and the data were averaged to give 2444 unique observed reflections ($|F_o| > 3\sigma(F)$).

Structure Determination

The copper atom was located on the origin and the positions of all remaining non-hydrogen atoms were determined from subsequent Fourier syntheses and block-diagonal least-squares calculations. A difference-Fourier map based on the anisotropic refinement revealed coordinates of all the hydrogen atoms. Atomic scattering factors for Cu^{2+} and Cl^- ions and S, C, N, O, and H atoms were taken from ref. [8]. The weighting scheme $\omega = 1/[\sigma^2(F_o) + 0.0005(F_o)^2]$ was introduced in the later stages of the refinement. The final refinement with anisotropic thermal parameters for all the non-hydrogen atoms and with isotropic thermal parameters for hydrogen atoms led to the residual indices $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.044$, $R' = [\Sigma\omega(|F_o| - |F_c|)^2/\Sigma\omega|F_o|^2]^{1/2} = 0.057$. Final atomic coordinates and anisotropic temperature factors are given in Table I. Observed and calculated structure factors are available from the Editor. All crystallographic calculations were performed on an ACOS 900S computer at the Crystallographic Research Center, Institute for Protein Research, Osaka University. Figure 1 was drawn according to the local version of the ORTEP-II program [9].

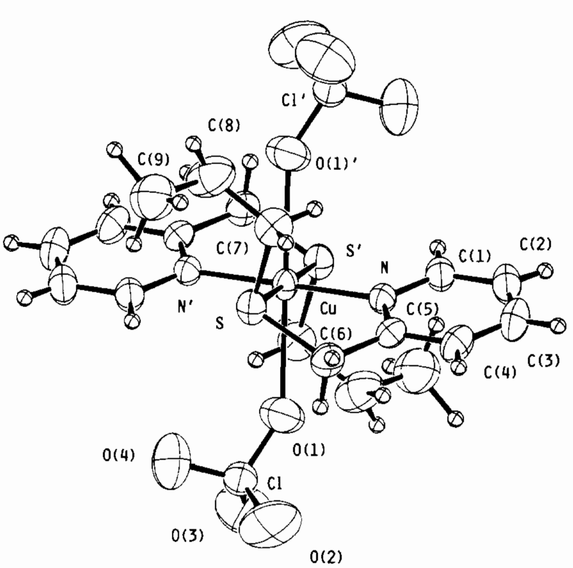

Fig. 1. Molecular structure of $[Cu(Pr^nSCH_2py)_2][ClO_4]_2$ (*6*) with the atom labelling scheme.

Results and Discussion

Description of the Structure of Bis[2-(n-propylmercaptomethyl)pyridine] copper(II) Diperchlorate (6)

The crystal structure consists of a discrete centrosymmetric molecule in a unit cell. Figure 1 shows the molecular geometry with the atom labelling scheme. The bond distances and angles are summarized in Table II. The pyridyl nitrogen and the sulfur atoms are coordinated to the copper ion to form a strictly planar *trans*-CuN_2S_2 unit, and the perchlorate oxygen atoms are bound in apical positions. This geometry around copper(II) ion is analogous to those of

TABLE III. Electronic Absorption Maxima, ESR Parameters, and $E^{0'}$ Values of the $Cu^{II}N_2S_2$ Complexes.

Complex	λ_{max}[a]/nm			$\lvert A_{\parallel}\rvert$[b]$/10^{-4}$ cm^{-1}	$g_{\parallel}$[b]	$g_{\perp}$[b]	$E^{0'}$[c]/V
	Cu ← N	Cu ← S	d–d				
1	264	348	610	154	2.23	2.07	0.49
2	264	330, 367	602, 680	156	2.22	2.07	0.55
3	260	360	597	176	2.17	2.04	0.44
4	266	390	622	157	2.19	2.07	0.66
5	265	388	628	164	2.20	2.07	0.68
6	266	388	634	160	2.19	2.07	0.69
7	266	398	640	157	2.19	2.05	0.72
8	268	394	642	151	2.27	2.04	0.73
9	d	340	624	132	2.24	2.04	0.28
10	d	381	583	150	2.28	2.07	0.37
11	d	391	590	147	2.28	2.08	0.41
12	d	395	596	153	2.28	2.08	0.43
13	260	372	574	153	2.17	2.05	0.33

[a] Measured in CH_3CN at 25 °C. [b] Measured in $CH_3NO_2/(CH_3)_2CO$ (1:1 v/v) for *1–8* and *13*, and in CH_3OH/C_2H_5OH (1:4 v/v) for *9–12* at 77 K. [c] Measured in CH_3CN containing 0.1 mol dm^{-3} [$Bu_4{}^nN$] [BF_4]. [d] Obscured by the π–π^* bands of ligands.

bis[(4-(n-propylmercaptomethyl)imidazole]copper(II) diperchlorate (*10*) [1] and bis(β-methylmercaptoethylamine)copper(II) diperchlorate (*13*) [7]. The Cu–S distance [2.366(1) Å] is somewhat shorter than that [2.396(2) Å] [1] of the corresponding imidazole complex (*10*). On the other hand, the Cu–N distance [2.015(3) Å] of the present complex is significantly longer than that [1.939(6) Å] [1] of *10*. This is consistent with the fact that the pyridyl nitrogen atom has a σ-donor ability smaller than the imidazolyl nitrogen as supported by the small pK_a value of pyridine compared with imidazole [10]. It is notable that the Cu–O distance [2.501(3) Å] is markedly shorter than that [2.594(6) Å] [1] of *10*, as well as that of various complexes of the [CuX_4][ClO_4]$_2$ type (X_4 = N_4, S_2N_2, or S_4 centers; 2.53–2.68 Å) [7, 11–13]. The strong Cu–O bonding in the present complex is consistent with a great localization of the positive charge on the copper atom owing to an important charge-transfer from copper to the pyridyl ligand which has a π-acceptor property larger than the imidazolyl ligand. The Cl–O bond length involving the coordinated oxygen atom [1.449(3) Å] is much longer than the other three Cl–O distances [1.403(5), 1.409(4), and 1.411(3) Å].

Redox Behavior, and Electronic Absorption and Electron Spin Resonance Spectra

Table III summarizes electrochemical and spectroscopic parameters for the $Cu^{II}N_2S_2$ complexes. All the complexes are subject to quasi-reversible electrochemical reductions to copper(I) species in acetonitrile containing [$Bu_4{}^nN$][BF_4] (0.1 mol dm^{-3}) as a supporting electrolyte. Redox potentials [$E^{0'} = (E_{pc} + E_{pa})/2$] of the present complexes are more positive than those of planar complexes of the $Cu^{II}N_4$, $Cu^{II}O_4$ and $Cu^{II}N_2O_2$ types with a tetradentate or two bidentate ligands, and are rather close to those of blue (type I) copper proteins ($E^{0'}$ = 0 to +0.6 V *vs.* SCE) [14]. Complexes *1–8* with the pyridyl donor show apparently more positive redox potentials than complexes *9–13* with the imidazolyl and amino groups. The increasing order of the $E^{0'}$ values for the complexes is consistent with the order of the increasing π-acceptor ability of the nitrogen-containing ligand; amino < imidazolyl < pyridyl groups [10], except for *9*. Since the redox potentials of the Cu^I/Cu^{II} systems depend on the relative stabilities of Cu^I- and Cu^{II}-complexes [15], the larger π-acceptor ability of the nitrogen-containing ligands would stabilize the Cu^I-state more than the Cu^{II}-state in the present complexes.

All the $Cu^{II}N_2S_2$ complexes exhibit electronic absorption bands around 260 nm and 380 nm (Table III), which are reasonably assigned to nitrogen-to-copper and sulfur-to-copper charge-transfer transitions, respectively [1]. Although no simple correlation has been observed between the wave number of these band maxima and the $E^{0'}$ value, there is a linear relation between the wave number of d–d band maxima (ν_{d-d}) and the $E^{0'}$ value for these $Cu^{II}N_2S_2$ complexes except for *3* and *9*, as shown in Fig. 2. The deviation of *3* and *9* from the ν_{d-d}–$E^{0'}$ plot may be related with the configurational change of the $Cu^{II}N_2S_2$ moiety of these complexes; complex *3* was reported to involve the $Cu^{II}N_2S_2$ moiety greatly distorted toward a square pyramid [16], and complex 9 seems to have the $Cu^{II}N_2S_2$ skeleton distorted toward a tetrahedral geometry based on its significantly small $\lvert A_{\parallel}\rvert$ value [1]. Thus, the linear relation between $E^{0'}$ and ν_{d-d} suggests

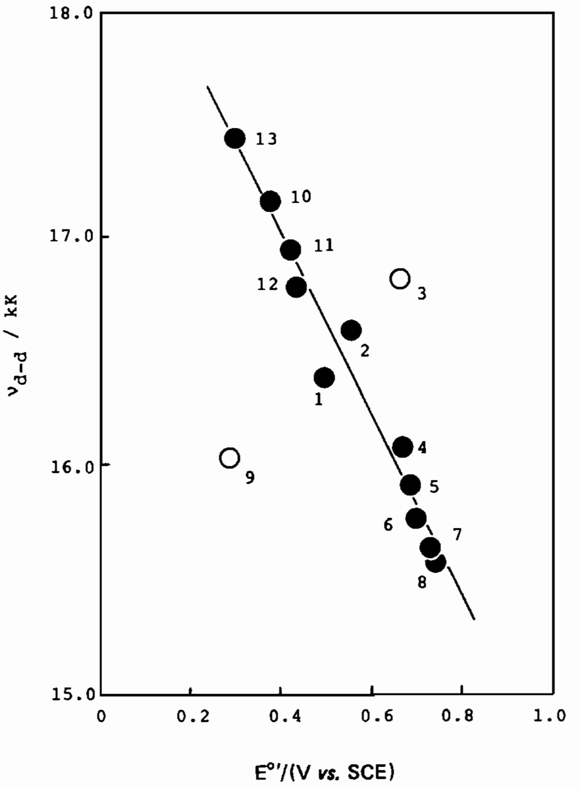

Fig. 2. A plot of the wave number of d–d band maxima (ν_{d-d}) *vs.* the $E^{0'}$ value of the $Cu^{II}N_2S_2$ complexes in CH_3CN at 25 °C.

that the electrochemical reduction may occur at the same orbital, $d_{x^2-y^2}$, of the Cu^{II} ion for the present complexes other than *3* and *9*. This is consistent with the ESR parameters; $g_\parallel > g_\perp \cong 2.07$ (Table III) [17]. The $g_\parallel$ values of complexes *1–13* are compared to those (2.19–2.30) of blue copper proteins [14]. Although ESR parameters for some $Cu^{II}N_2S_2$ complexes have been examined [16, 18, 19], no simple correlation has been found between $|A_\parallel|$ and $g_\parallel$ values. The plot of $|A_\parallel|$ *vs.* $g_\parallel$ for the present complexes, however, show an approximate linear relation with the exceptions of *3* and *9* with different geometry again, as depicted in Fig. 3.

In the square planar copper complexes with N_4, N_2O_2, or O_4 donor set, the increase of delocalization of the unpaired spin density away from the copper nucleus has been reported to cause the increase of $|A_\parallel|$ and the simultaneous decrease of $g_\parallel$ values [20]. The present correlation between $|A_\parallel|$ and $g_\parallel$ may therefore reflect the delocalization of the unpaired spin density.

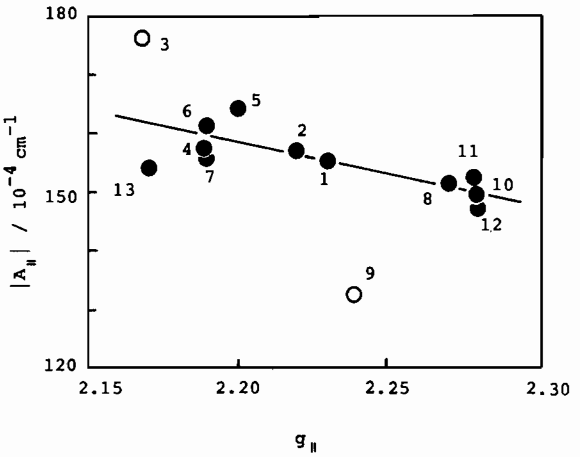

Fig. 3. A plot of the $|A_\parallel|$ *vs.* the $g_\parallel$ value for the Cu^{II}-N_2S_2 complexes in $CH_3NO_2/(CH_3)_2CO$ (1:1 v/v) (*1–8* and *13*) and in CH_3OH/C_2H_5OH (1:4 v/v) (*9–12*) at 77 K.

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