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Structure of Cu(II) Complexes of Pyridine-2,6-dithiocarbomethylamide

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The crystal structure of the paramagnetic pyridine-2,6-dithiocarbomethylamide—copper(II) chloride (Cu*PDTA*-Cl_2) is described: $C_9H_{11}N_3S_2CuCl_2 \cdot H_2O$, monoclinic, $P2_1/n$, $a = 9.163$ (2), $b = 8.925$ (5), $c = 17.590$ (9) Å, $\beta = 102.08$ (1)°, $Z = 4$, $d_x = 1.784\,g\,cm^{-3}$. The structure was refined to a residual of $R = 0.059$. The copper is coordinated in a square—pyramidal arrangement by the pyridine nitrogen, the two thioamide sulfur atoms and the two chloride ions. The shortest Cu—Cu distance in the crystal is 5.02 Å, leading to only very weak antiferromagnetism. Spectroscopic and magnetic data are given for additional members of the Cu*PDTA*-*X* [$X = Cl_2$, Br_2, I_2, $(NO_3)_2$, $(SCN)_2$, *Py*] complex type, which suggest a large degree of structural resemblance with the Cu*PDTA*-Cl_2 complex.

[Keywords: Crystal structure analysis; Electronic spectra; Infrared spectra; Magnetic susceptibility; Pyridine-2,6-dithiocarbomethylamide copper(II)]

Struktur von Kupfer(II)-Komplexen des Pyridin-2,6-dithiocarbomethylamids

Die Kristallstruktur des paramagnetischen Pyridin-2,6-dithiocarbomethylamid Kupfer(II)-chlorids wurde bestimmt: $C_9H_{11}N_3S_2CuCl_2 \cdot H_2O$, monoklin, $P2_1/n$, $a = 9{,}163$ (2), $b = 8{,}925$ (5), $c = 17{,}590$ (9) Å, $\beta = 102{,}08$ (1)°, $Z = 4$, $d_x = 1{,}784\,g\,cm^{-3}$. Die Struktur wurde bis zu einem *R*-Faktor von $R = 0{,}059$ verfeinert. Das Kupfer-Zentralatom zeigt quadratisch-pyramidale Koordination durch den Pyridin-Stickstoff, die beiden Thioamid Schwefelatome sowie zwei Chloridionen. Der kürzeste Cu—Cu-Abstand im Kristall beträgt 5,02 Å, was zu einem nur sehr schwachen Antiferromagnetismus führt. Spektroskopische und magnetische Größen werden für weitere Derivate vom Cu*PDTA*-*X* Typ [$X = Cl_2$, Br_2, I_2, $(NO_3)_2$, $(SCN)_2$, Pyridin] angegeben, und im Sinne einer großen strukturellen Ähnlichkeit mit dem Cu*PDTA*-Cl_2 interpretiert.

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Introduction

Pyridine-2,6-dithiocarbomethylamide (*PDTA*) can form a 1:1 and a 1:2 complex with copper(II)[1]. Spectroscopic evidence suggests, that the 1:2 complex is structurally similar to the quasi-octahedral $Ni(PDTA)_2(NO_3)_2$ complex, whose crystal structure is known[2]. The present communication deals with the 1:1 complex type [Cu*PDTA*-*X*, $X = Cl_2$, Br_2, I_2, $(SCN)_2$, $(NO_3)_2$, *Py*]. We have determined the crystal structure of the Cu*PDTA*-Cl_2 complex in view of its interesting orientation-dependent single crystal ESR-spectrum[3]. Knowledge of the Cu*PDTA*-Cl_2 crystal structure permits spectroscopically based structural extrapolations to other members of this complex type.

Experimental

X-Ray Analysis: Blue-green crystals, obtained from aqueous solution[1], appeared in the form of elongated rhombohedral prisms. A specimen with dimensions 0.2 × 0.1 × 0.1 mm was used for the structure analysis, which was carried out with the help of a locally modified *Stoe* 4-circle diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.71069$ Å). Cell dimensions were obtained by last-squares from the setting angles of 12 carefully centered reflections, whose approximate positions had previously been obtained from a random peak search. The monoclinic symmetry was subsequently checked with several precession-photographs.

Intensities of all reflections within $2\theta \leq 50°$ ($\sin\theta/\lambda \leq 0.595$) were determined in the ω-scan mode (scan width: $\Delta\omega = 1.4°$), using variable scan speed to optimize data collection time. The 2473 independent reflections were processed in the usual way to yield 1163 non-zero structure factors [$I_0 > 2\sigma(I_0)$]. No absorption correction was applied [$\mu(\mathrm{MoK}\alpha) = 22.6\ \mathrm{cm}^{-1}$].

The structure solution involved direct methods (Multan 80[4]) to localize the position of the metal atom; the remaining non-hydrogen atoms were obtained by difference *Fourier* techniques (SHELX[5]). Least-squares refinement was carried to the level of anisotropic temperature factors for all atoms except hydrogen. For the *PDTA* moiety, hydrogen atoms were included at calculated positions, while the locations of the water protons were observed in a difference *Fourier* synthesis. In the last refinement cycles, hydrogen atoms were refined with individual isotropic temperature factors, with the exception of the methyl groups, which were refined as rigid groups with a common isotropic temperature factor for all protons bonded to the same carbon atom. The positions of the remaining protons were constrained to a stereochemically reasonable distance from the atom to which they are bonded.

Refinement was terminated at a residual of $R = 0.059$ [199 parameters, 1253 contributing observations, weighting system $w_i = k/(\sigma^2(F_0)_i + gF_{0i}^2)$; $k = 0.915$, $g = 0.0071$]. A final difference *Fourier* synthesis showed a highest peak of 0.7 eÅ^{-3} in the immediate vicinity of the copper atom.

Spectra and Magnetic Data: Magnetic susceptibilities were determined with a *Paar* SUS 10 instrument, which uses a modified *Faraday* technique. The instrument was calibrated with a $Hg[Co(NCS)_4]$ standard. Measurements were carried out in a temperature range between 300 and 80 K under a 50 Torr helium atmosphere. Experimental diamagnetic corrections were applied for the *PDTA* ligand[2], whereas the diamagnetic corrections for the metal and the anions were taken from the literature[6]. No TIP correction was applied. Infrared spectra were obtained as nujol mull on a Perkin-Elmer 580 B, far infrared spectra on a Beckmann 725 FS, diffuse UV/VIS reflectance spectra (DRS) on a Cary 17 D instrument.

Results and Discussion

Crystal Structure

Table 1 lists atomic coordinates and isotropic tensor components; for non-hydrogen atoms, which had been refined anisotropically, equivalent isotropic tensor components are given, which were calculat-

Table 1. *Fractional atomic coordinates and equivalent isotropic tensor components ($\times 10^4$, U values in Å^2). E.s.d.'s are in units of the last significant figure. Note that the e.s.d.'s for H-atoms are underestimated as a result of positional constraints (see text)*

Atom	X/a	Y/b	Z/c	Ueq or U
CU	829 (2)	1805 (2)	4083 (1)	305 (8)
Cl-1	963 (4)	1826 (4)	2626 (2)	400 (18)
Cl-2	2176 (4)	3822 (3)	4567 (2)	434 (18)
S-1	-1388 (4)	3072 (4)	3971 (2)	412 (19)
S-2	2769 (4)	191 (3)	4517 (2)	394 (19)
N-1	-3940 (11)	1850 (12)	3306 (6)	366 (58)
N-2	2569 (11)	-2673 (12)	4159 (7)	346 (63)
N-3	-428 (10)	-42 (9)	3871 (5)	224 (51)
C-1	-2532 (12)	1647 (13)	3593 (6)	261 (60)
C-2	1852 (14)	-1406 (12)	4184 (7)	285 (63)
C-3	-1916 (13)	89 (12)	3601 (7)	260 (68)
C-4	192 (13)	-1402 (12)	3909 (7)	257 (59)
C-5	-2830 (14)	-1160 (13)	3392 (8)	338 (68)
C-6	-637 (15)	-2703 (13)	3742 (8)	336 (74)
C-7	-2167 (15)	-2571 (16)	3473 (9)	418 (80)
C-8	-4719 (17)	3335 (17)	3273 (9)	496 (82)
C-9	4178 (14)	-2866 (17)	4422 (8)	450 (81)
O	3819 (11)	346 (11)	2334 (7)	571 (70)
H (N-1)	-4660 (94)	1038 (87)	2997 (50)	271 (284)
H (N-2)	2226(158)	-3534(137)	3737 (56)	672 (478)
H (C-5)	-4020 (21)	-1015 (99)	3164 (46)	1 (226)
H (C-6)	-226(146)	-3798 (71)	3943 (80)	756 (481)
H (C-7)	-2890(103)	-3520 (78)	3296 (62)	277 (327)
H1 (C-8)	-4502 (17)	4153 (17)	3735 (9)	1429 (575)
H2 (C-8)	-5844 (17)	2915 (17)	3210 (9)	1429 (575)
H3 (C-8)	-4592 (17)	3852 (17)	2736 (9)	1429 (575)
H1 (C-9)	4229 (14)	-2353 (17)	4983 (8)	2001(1038)
H2 (C-9)	4708 (14)	-2141 (17)	4069 (8)	2001(1038)
H3 (C-9)	4750 (14)	-3931 (17)	4498 (8)	2001(1038)
H1 (O)	3070(105)	714(124)	2637 (52)	443 (311)
H2 (O)	3631(125)	-622 (69)	2044 (59)	625 (337)

ed as one third of the trace of the orthogonalized u_{ij}-tensor. A visual impression of the anisotropicity of these atoms can be obtained from Fig. 1. which shows the vibrational ellipsoids at the 50% level (XRAY[7]). Fig. 2 gives intramolecular bondlengths and bond angles. Fig. 3 shows a stereoscopic packing diagram.

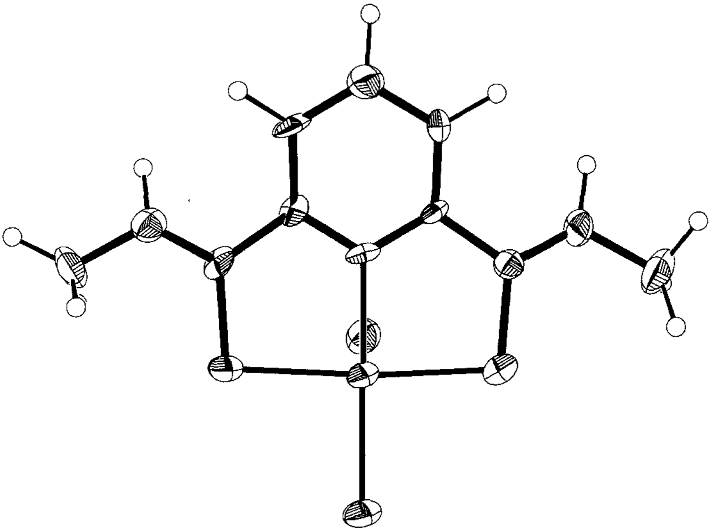

Fig. 1. Projection of the Cu*PDTA*-Cl_2 moiety into the pyridine ring plane. Ellipsoids are drawn at the 50% probabitity level, with the exception of hydrogen atoms, which were drawn artificially small

The copper atom has a distorted square-planar coordination by the pyridine nitrogen N-2. the two thioamide sulfur atoms and the chlorine Cl-2. This square planar arrangement is slightly distorted towards square-pyramidal as result of the coordination of the second chlorine atom Cl-1. The length of the Cu—Cl1 distance and the small deviation of Cu from a plane trough the four other ligand atoms (0.28 Å) indicate that Cl-1 is only rather weakly coordinated to the metal atom. This agrees with the situation in other 5-coordinated Cu(II)complexes[8]; we also note that one Cl atom dissociates in solution[1].

The intramolecular bonding parameters (Fig. 2) are in keeping with the chemical constitution. Compared to the free *PDTA* ligand[9] and the Ni(*PDTA*)$_2$(NO_3)$_2$ crystal structure. the two thioamide groups show a lengthening of the C—S bonds and a slight shortening of the C—N bonds: the corresponding values (averaged over the two groups) are:

PDTA: C—N, 1.316 (3), C—S, 1.669 (3); Ni$(PDTA)_2(NO_3)_2$: C—N, 1.316 (10), C—S, 1.669 (9); Cu*PDTA*-Cl_2: C—N, 1.305 (10), C—S, 1.694 (8). Although this correlation is on the verge of statistical significance, it is in good agreement with the ir evidence. Thus, the ir band positions for the ν(C—N) stretching vibrations of the thioamide groups show a shift towards higher frequencies in the sequence: *PDTA* (1 535 cm^{-1}), Ni $(PDTA)_2(NO_3)_2$ (1 562 cm^{-1}) and Cu*PDTA*-Cl_2 (1 585 cm^{-1}).

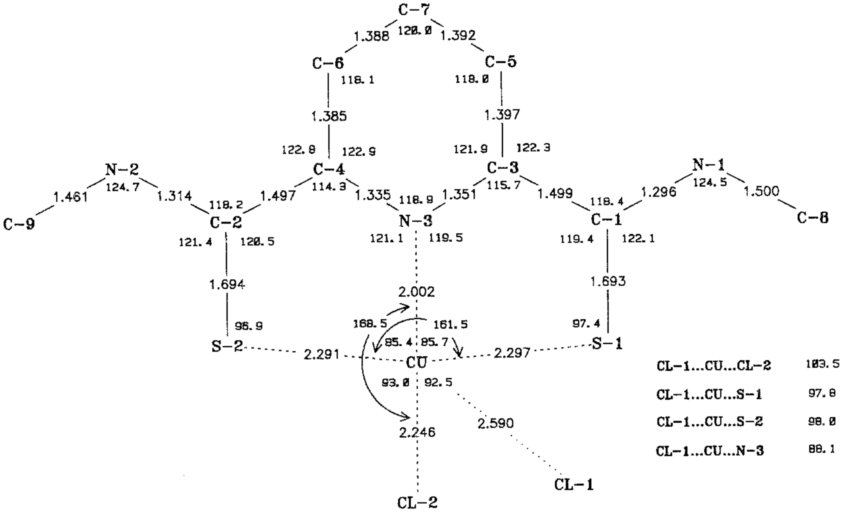

Fig. 2. Bonding parameters for the Cu*PDTA*-Cl_2 crystal structure. The approximate standard deviation are as follows: Bond length: Cu—S, Cu—Cl: 0.004 Å; Cu—N: 0.008 Å; C—S: 0.011 Å; C—N, C—C: 0.015 Å. Bond angles: 0.5-1.5° for non-hydrogen atoms

The torsion angles between the pyridine ring and the thioamide groups (Cu*PDTA*-Cl_2: N3-C4-C2-N2, —172°; N3-C3-C1-N1, 177°) indicate the same small degree of non-planarity in all three *PDTA* crystal structures.

In the Cu*PDTA*-Cl_2 crystal, pairs of antiparallel molecules related by an inversion center (Fig. 3) are crosslinked by hydrogen bonds from the solvated water molecule to the chlorine Cl-1 and the two thioamide protons: H1(O)...$Cl\text{-}1_{x,y,z}$: 2.17 (10) Å; H2(O)...$Cl\text{-}1_{1/2-x,y-1/2,1/2-z}$: 2.36 (6) Å; O...H$(N\text{-}1)_{1+x,y,z}$: 1.73 (8) Å; O...H$(N\text{-}2)_{1/2-x,1/2+y,1/2-z}$: 2.17 (10) Å. The shortest Cu—Cu distance in the crystal (5.02 Å) is observed between molecules forming a

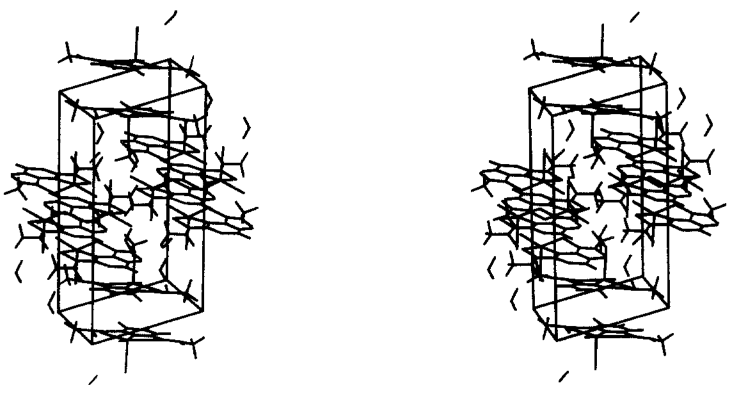

Fig. 3. Stereoscopic packing diagram of the crystal structure of Cu*PDTA*-Cl_2

centrosymmetric 'dimer'; although this value precludes considerable Cu—Cu interactions, it is not in disagreement with the weak antiferromagnetism observed for this material.

Spectra and Magnetic Data

Fig. 4 shows the diffuse reflectance spectra of several complexes of the Cu*PDTA*-*X* type. The known coordination geometry for Cu*PDTA*-Cl_2 suggests, that the broad asymmetric maximum at 13.60 kK results from a supperposition of the $d_{xz}(d_{yz}) \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ transitions[8]. This is consistent with the ESR spectrum, which suggests a $d_{x^2-y^2}$ ground state[3]. The similarity in the electronic spectra of the other members of this complex type indicate a comparable microsymmetry around the copper atom. The hypsochromic shift (with respect to Cu*PDTA*-Cl_2) (Table 2) can be interpreted in terms of a spectrochemical series, with a square-planar Cu*PDTA*-*Py* end point.

For all compounds the temperature dependence of the magnetic susceptibility between 300 and 80 K follows a *Curie-Weiss* law of the form $\mu = 2.828[X_A(T + \theta)]^{1/2}$. Values for μ and θ (derived from a $1/X$ vs. T regression) are also listed in Table 2. These values indicate that all compounds must be regarded as magnetically diluted systems, some of which possibly show weak antiferromagnetism. The lowest *Weiss* constant ($\theta = -10$ K) is observed for Cu*PDTA*-Cl_2, for which the smallest Cu—Cu distance in the crystal is 5.02 Å.

Table 2 also lists the ir band positions in the metal-ligand stretching mode region. Undoubtedly, all Cu-complexes show coordination via the

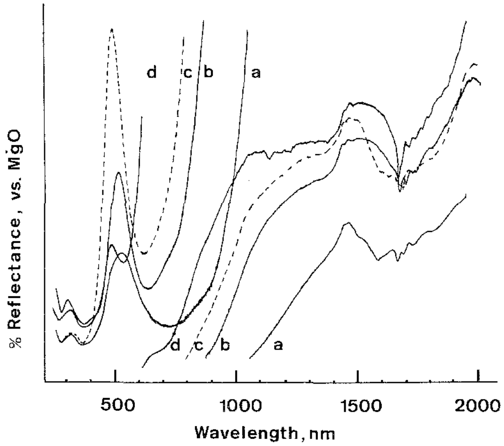

Fig. 4. Diffuse reflectance spectra for different Cu*PDTA*-complexes. *a* Cu*PDTA*-Cl_2; *b* Cu*PDTA*-Br_2; *c* Cu*PDTA*$(NO_3)_2$; *d* Cu*PDTA*-*Py*

thioamide sulfur atoms and the pyridine nitrogen. In addition, at least one anion is also strongly coordinated to the metal atom. Bands at 1 495 cm^{-1} ($\nu_a NO_2$), 1 389 cm^{-1} ($\nu_a NO_2$) and 1 282 cm^{-1} ($\nu_s NO_2$) indicate, that in Cu*PDTA*$(NO_3)_2$ one NO_3^--anion acts as a bridging bidentate. The Cu*PDTA*$(SCN)_2$ complex has at least one SCN group coordinated via nitrogen [ν(CN): 2 078/2 108 cm^{-1}, ν(CS): 820 cm^{-1}, ν(NCS): 472 cm^{-1}].

The compiled crystallographic, spectroscopic and magnetic evidence therefore suggests, that all the above Cu(II) complexes show a high degree of structural resamblance.

Table 2. *Spectroscopic and magnetic data for different* Cu(II)PDTA *complexes (preparation see*[1]*). DRS: diffuse reflectance maxima (kK);* μ, θ*: effective magnetic moment (B.M.) and Weiss constant (K) (see text);* ν*: ir band positions (cm*$^{-1}$*)*

Compound	DRS	μ	θ	ν(Cu-S)	ν(Cu-N)	ν(Cu-X)
Cu*PDTA*-Cl_2	13.30	1.80	—10	341/356	260/273	297/313
Cu*PDTA*$(SCN)_2$	15.20	1.75	—9	355	275	314
Cu*PDTA*-Br_2	15.65	1.90	—6	357/362	264/275	230/217
Cu*PDTA*-I_2	16.20	1.87	—4	371	255/270	170/183
Cu*PDTA*$(NO_3)_2$	16.20	1.81	—4	368	280/319	220
Cu*PDTA*-*Py*	18.60 13.80 sh	1.78	—7	367	278/310	250

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References

[1] *Gagliardi E.*, *Popitsch A.*, Monatsh. Chem. **103**, 1337 (1972).

[2] *Kratky C.*, *Schurz J.*, *Gagliardi E.*, *Popitsch A.*, Monatsh. Chem. **112**, 721 (1981).

[3] *Popitsch A.*, *Feichtinger H.*, *Czaputa R.*, to be published.

[4] *Germain G.*, *Main P.*, *Woolfson M. M.*, Acta Cryst. **A 27**, 368 (1971).

[5] *Sheldrick G. M.*, SHELX 76, a program for crystal structure determination, University of Cambridge, England.

[6] *Weiss A.*, *Witte H.*, Magnetochemie. Verlag Chemie. 1972.

[7] *Stewart G. M.*, The XRAY System-Version of 1976. Technical Report TR-466, CSS. University of Maryland, U.S.A.

[8] *Hathaway B. J.*, *Billing D. E.*, Coordin. Chem. Rev. **5**, 143 (1970).

[9] *Popitsch A.*, *Gagliardi E.*, *Schurz J.*, *Kratky C.*, Monatsh. Chem. **112**, 537 (1981).