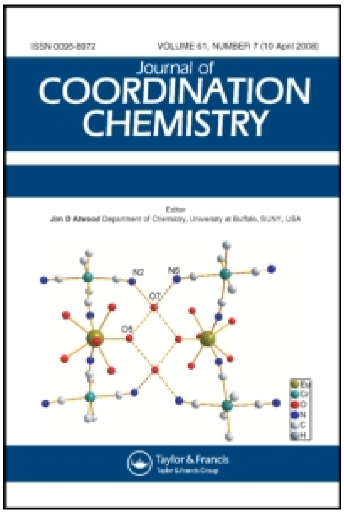

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CRYSTAL STRUCTURE DETERMINATION OF DICHLOROBIS(1-PHENYL-3,5-DIMETHYLPYRAZOLE)COPPER(II) - [$CuCl_2(pdmp)_2$]

R. H. P. Francisco[a]; J. R. Lechat[a]; A. C. Massabni[b]; C. B. Melios[b]; M. Molina[b]
[a] Instituto de Física e Química de São Carlos (USP), São Carlos, S.P., Brasil [b] Instituto de Química de Araraquara (UNESP), Araraquara, S.P., Brasils

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CRYSTAL STRUCTURE DETERMINATION OF DICHLOROBIS(1-PHENYL-3,5-DIMETHYLPYRAZOLE)COPPER(II) – [$CuCl_2(pdmp)_2$]

R. H. P. FRANCISCO and J. R. LECHAT

Instituto de Física e Química de São Carlos (USP) C.P. 369 – 13.560 São Carlos, S.P., Brasil

A. C. MASSABNI, C. B. MELIOS and M. MOLINA

Instituto de Química de Araraquara (UNESP) C.P. 174–14.800 Araraquara, S.P., Brasil

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The crystal structure of dichlorobis (1-phenyl-3,5-dimethylpyrazole)copper(II), [$CuCl_2(pdmp)_2$],$CuCl_2C_{22}H_{24}N_4$, monoclinic, $P2_1/c$, a = 13.121(5), b = 10.610(2), c = 13.973(5) Å, β = 145.51(1)°, Z = 2, D_m = 1.44 (flotation), D_x = 1.44 g.cm^{-3}, μ(CuKα) = 37.6 cm^{-1}, has been determined from three dimensional X-ray diffractometric data. The structure was solved by direct methods and refined by full-matrix least-squares calculations to R = 0.060 using 2072 reflexions for which $I > 3\sigma(I)$. The copper atom is tetracoordinated and the stereochemistry around it is *trans*-square planar. The relevant distances are Cu–Cl 2.268(1) and Cu–N 1.979(1) Å. Spectral and magnetic properties of the complex are reported and their relations with the present structural data are discussed.

INTRODUCTION

Structural studies on Cobalt(II), Nickel(II), Copper(II) and Silver(I) complexes with 1-phenyl-3,5-dimethylpyrazole(pdmp) are in progress in our laboratories[1-4] with the main purpose of comparing the configurations of such compounds with those of complexes involving closely related pyrazole derivatives. Single-crystal X-ray studies on two metal-pdmp complexes have been completed.[5,6]

For the most part of $CuCl_2L_2$ complexes (L = pyrazole-derived ligands), polymeric structures with tetragonal six-coordination about copper achieved by chloride bridges have been assigned.[7-9] However, the features shown by the electronic spectrum of [$CuCl_2(pdmp)_2$] are not consistent with the named structures nor with those of dimeric units in which the copper(II) ion is pentacoordinated.[10,11] Hence, an X-ray investigation of the title complex was undertaken in order to elucidate its structural situation.

Experimental

[$CuCl_2(pdmp)_2$] was obtained by mixing hot ethanolic solutions of $CuCl_2 \cdot 2H_2O$ and pdmp in the molar proportion M : L of 1 : 2. On cooling at room temperature the dark green crystalline compound began to separate. The solid was filtered and washed three times with cold solvent. Ethanol was also used for recrystallization. The crystals were elongated blocks (0.2 mm x 0.1 mm x 0.08 mm) with prismatic habit. All X-ray experiments were performed using a single crystal CAD-4 automatic diffractometer with graphite-monochromated CuK α radiation (λ = 1.5418 Å). The unit cell was determined on the basis of 25 strong reflexions found by mounting the crystal at random, with the detector position varying between θ = 10° and θ = 60°. The unit cell was found to be monoclinic and the experimental density (1.44 g.cm^{-3}) determined by flotation, in a mixture of carbon tetrachloride and benzene, is in agreement with that calculated for Z = 2 (1.44 g.cm^{-3}). Precise lattice parameters and their standard deviations were determined by means of least-squares calculation minimizing $\Sigma(\sin\theta_c - \sin\theta_0)^2$ for the 25 reflexions cited above. They are: a = 8.073(2), b = 10.610(2), c = 13.121(5) Å, β = 101.46(1)°, V = 1101(1) Å.^{3} The $\omega - 2\theta$ scan technique was used to record the intensities for all reflexions for which $0° < \theta < 75°$. Scan widths were calculated from the formula sw = 1.° + 0.142° tan θ. This calculated scan angle was extended at each side by 25% for background determination. From the 2269 unique reflexions thus considered, the 2072 having net intensity greater than $3\sigma(I)$ (σ = standard error based on count statistics) were used in structure determination and refinement. Every two hours three standard reflexions were monitored to check the crystal stability. Only statistical variations were observed. Lorentz and polarization corrections were applied but no absorption correction was made [$\mu(\mathrm{CuK}\alpha) = 37.6\ \mathrm{cm}^{-1}$]. The systematic extinctions were consistent with the space group $P2_1/n$.

Electronic spectra in solution (25.0 – 6.7 kK range) at 25.0 ± 0.1 °C were recorded on a Cary mod. 17 spectrophotometer using matched silica cells, with the pure solvent as a reference. Magnetic moments of the solid complexes were determined at room temperature (26 °C) by the Gouy method. The values have been corrected for the diamagnetic susceptibilities of the ligands in the usual way.[12]

Solution and Refinement of the Structure

The structure was solved by direct methods (MULTAN)[13] in the space group $P2_1/n$. The overall temperature factor and absolute scale were estimated from a Wilson plot. The distribution of the E's was in good agreement with the theoretical centrosymmetric values. The phases of the reflexions $(1\ 11\ \bar{4})$, $(1\ 9\ 1)$ and $(6\ 1\ 9)$ were chosen to fix the origin and three other reflexions $(0\ 4\ 8)$, $(4\ 6\ 8)$ and $(3\ 6\ 11)$ were used in the starting set. The E-map computed with the chosen MULTAN solution (ABS FOM = 1.0239, RESID = 20.10, COM FOM = 3.0000) showed a chemically reasonable structural fragment consisting of Cu(II), the Cl^- and the pyrazolic ring. The R factor calculated with these seven atoms was 0.30 after one cycle of refinement of the scale factor. All the refinements were made by full-matrix least squares method by minimization of $\Sigma\omega(k\,|F_0| - |F_c|)^2$, where $\omega = 1$ for the observed reflexions and $\omega = 0$ for the others. Subsequent difference – Fourier calculations led to the location of all non-hydrogen atoms. The refinement with isotropic temperature factors brought the R factor to 0.17. Anisotropic temperature factors were assigned to all the atoms. When the R factor became 0.08 the weighting scheme was changed to $\omega = \sigma(F_0)^{-2}$ for the observed reflexions and $\omega = 0$ for the others. After two cycles of refinement (R = 0.07) the hydrogen atomic positions were calculated and an isotropic temperature factor of 5.0Å^2 was assigned to them. The refinement was continued until all atomic parameters shifts were smaller than each standard deviation. The final unweighted R factor omitting unobserved reflexions was 0.060 and including them 0.061; the weighted R factor defined as $[\Sigma\omega(k\,|F_0| - |F_c|)^2/\Sigma\omega(k\,|F_0|)^2]^{1/2}$ was 0.059. Complex neutral-atom scattering factors were used.[14] Suitable transformations were performed to change the space group to $P2_1/c$, in order to refer the structure to a conventional space group. The new unit cell was: a = 13.121(5), b = 10.610(2), c = 13.973(5) Å, β = 145.51(1)°, V = 1101(1) Å.^{3} All computer calculations were performed using the Enraf Nonius Structure Determination Package.

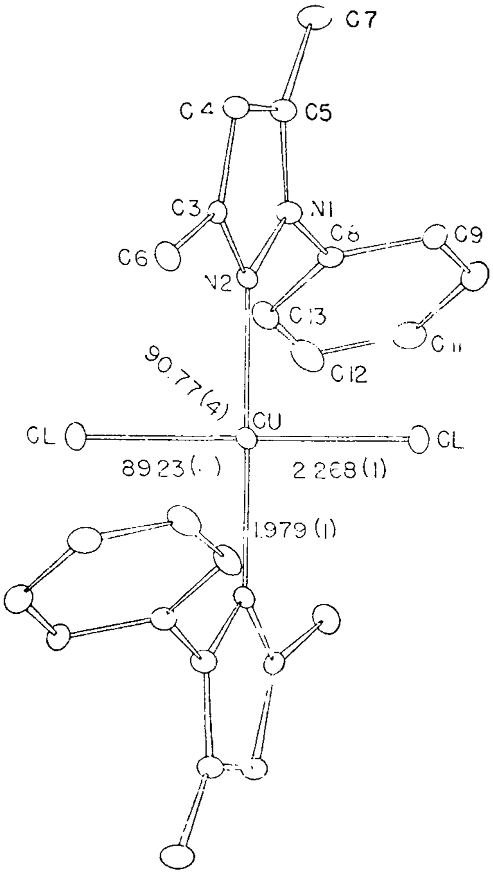

FIGURE 1. View of the molecule with distances (Å) and angles (°) around the metal with their e.s.d.'s in parentheses.

Figure 1 was drawn with the ORTEP Fortran plot program.[15] The final atomic parameters are given in Table I.

Results and Discussion

The structure is built up of isolated $\mathrm{CuCl_2(C_{11}H_{12}N_2)_2}$ units and the copper ion is

TABLE I

Fractional atomic coordinates (x 10^5) for chloride and (x 10^4) for the others. Anisotropic thermal parameters (x 10^5) for copper and chloride ions and (x 10^4) for the other non-hydrogen atoms. Estimated standard deviations are in parentheses.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu1	0	0	0	1383(3)	402(4)	1202(2)	35(4)	2302(3)	3(4)
Cl1	18714(6)	9045(6)	25314(5)	2125(4)	764(6)	1453(3)	-356(8)	3007(4)	-470(7)
N1	-1434(2)	2602(2)	-1367(2)	142(1)	48(2)	137(1)	21(2)	245(1)	24(2)
N2	-371(2)	1672(2)	-883(1)	148(1)	45(2)	133(1)	14(2)	247(1)	9(2)
C3	456(2)	2138(2)	-1016(2)	150(1)	64(2)	129(1)	1(3)	248(1)	-3(2)
C4	-104(2)	3368(2)	-1598(2)	182(1)	58(2)	156(1)	-10(3)	305(1)	7(2)
C5	-1311(2)	3653(2)	-1823(2)	168(1)	45(2)	141(1)	19(3)	267(1)	27(3)
C6	1733(2)	1351(3)	-592(2)	218(1)	74(2)	232(1)	-9(3)	416(1)	-39(3)
C7	-2418(3)	4812(3)	-2520(3)	245(2)	72(2)	252(2)	101(3)	449(2)	108(3)
C8	-2538(2)	2435(2)	-1391(2)	126(1)	55(2)	128(1)	19(3)	218(1)	31(3)
C9	-2300(2)	3223(3)	-429(2)	149(1)	85(2)	136(1)	-18(3)	246(1)	-9(3)
C10	-3428(2)	3092(3)	-500(2)	204(1)	92(3)	170(1)	37(3)	340(1)	34(3)
C11	-4730(2)	2168(3)	-1508(2)	199(1)	93(3)	236(1)	45(3)	395(1)	66(4)
C12	-4920(3)	1383(3)	-2427(3)	185(1)	82(3)	283(2)	-44(4)	407(2)	-36(4)
C13	-3855(2)	1520(3)	-2418(2)	172(1)	71(2)	200(1)	-42(3)	322(2)	-61(3)

The temperature factor expression used was $\exp-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})$.

coordinated by two chlorides and two nitrogen atoms of the organic ligands. Since the copper ion is situated on a center of inversion, the coordination has to be exactly planar and *trans*-square. The equation of the plane, referred to the conventional orthogonalized coordinates, is:

$$-0.9412x + 0.1648y - 0.2951z = 0 \qquad (1)$$

The stereochemistry of the copper ion is shown in Figure 1. The two rings of each organic ligand are planar within the standard deviations. The equations of the phenyl and pyrazole rings mean planes are respectively:

$$-0.0436x + 0.6462y - 0.7620z = 2.5858 \qquad (2)$$

$$0.0489x - 0.3300y - 0.9427z = 0.0968 \qquad (3)$$

The dihedral angles are: (1)–(2) : 68.1°, (1)–(3) : 79.8° and (2)–(3) : 59.8°.

All the bond distances and angles are given in Figure 1 and in Table II. They compare well with the values found in *tris*(1-phenyl-3,5-dimethylpyrazole)-silver(I) nitrate[5] and in dinitratebis(1-phenyl-3,5-dimethylpyrazole)copper(II)[6].

In $[Cu(NO_3)_2(pdmp)_2]$ the Cu–N distance is 1.989 Å (mean value). In $[CuCl_2(pdmp)_2]$ the Cu–N and the Cu–Cl bond lengths (1.979 and 2.268 Å respectively) are similar to the respective mean values reported for other Copper(II) chloride complexes: 1.976 and 2.350 Å in dichlorobis[1-(2-pyridylmethyl)imidazole] copper(II),[16] 2.00 and 2.23 Å in dichlorobis(2-methylpyridine)copper(II)[17] and 2.00 and 2.28 Å in dichlorobis(4-ethylpyridine)copper(II).[18]

The electronic spectrum of $[CuCl_2(pdmp)_2]$ in nitromethane solution exhibits three absorption bands: one very broad and asymmetrical, with its maximum located at 13.1 kK ($\epsilon = 86\ M^{-1}.\ cm^{-1}$) and two others, both sharp, with maxima at 7.1 kK ($\epsilon = 23\ M^{-1}.\ cm^{-1}$) and 6.8 kK ($\epsilon = 3\ M^{-1}.\ cm^{-1}$). Nitromethane was chosen because it proved to be the less coordinating solvent in which the complex still presents significant solubility. Moreover the named solvent presented convenient features in comparison with other common solvents in connection with spectroscopic studies on transition-metal complexes involving pyrazole derivatives.[7,19] The absorption maxima, their respective molar absorptivities and the magnetic moment (1.9 ± 0.1 B.M.) are consistent with the square-planar structure presently determined through X-ray data.[20-22]

It is interesting to note that for many $CuCl_2L_2$ complexes (L = pyridine, pyrazole and imidazole derivatives having no bulky substituents adjacent to

TABLE II

Bond distances (Å) and angles (°) with their e.s.d.'s.

N1–N2	1.349(2)	N2–N1–C5	111.3(1)
N1–C5	1.358(2)	N2–N1–C8	121.9(1)
N1–C8	1.433(2)	C5–N1–C8	126.8(1)
N2–C3	1.339(2)	N1–N2–C3	106.4(1)
C3–C6	1.489(2)	N1–N2–Cu1	126.2(1)
C3–C4	1.386(2)	Cu1–N2–C3	127.3(1)
C4–C5	1.370(2)	N2–C3–C4	109.4(1)
C5–C7	1.496(2)	N2–C3–C6	120.9(1)
C8–C9	1.382(2)	C4–C3–C6	129.8(1)
C8–C13	1.379(2)	C3–C4–C5	107.3(1)
C9–C10	1.406(2)	N1–C5–C4	105.8(1)
C10–C11	1.377(3)	N1–C5–C7	123.6(1)
C11–C12	1.370(3)	C4–C5–C7	130.5(1)
C12–C13	1.394(2)	N1–C8–C9	119.3(1)
		N1–C8–C13	119.1(1)
		C9–C8–C13	121.5(1)
		C8–C9–C10	119.4(1)
		C9–C10–C11	119.3(1)
		C10–C11–C12	120.3(1)
		C11–C12–C13	121.5(2)

the *N* donor site of the ligands) square-planar arrangements of two chloride and two nitrogen atoms with one or two distant chloride atoms (from adjacent copper centers) – completing distorted tetragonal pyramidal and octahedral structures, respectively – have been inferred on the basis of spectroscopic, magnetic and conductivity data.[8,9,23,24] Such assignments were confirmed in some cases by X-ray structure determinations.[10,11,17,25] In the present study bridging through chloride atoms has not been observed; the typical discrete *trans* square-planar structure is retained most probably owing to the presence of two phenyl radicals (bonded to the amine nitrogen atoms of the pyrazole rings) which introduce steric hindrance making the approach of chloride atoms from other units very difficult. Also, the absence of $\gt$NH groups in pdmp (these are, of course, present in amine nitrogen unsubstituted pyrazoles) rules out the possibility of hydrogen bonding between the named groups and chloride atoms. The occurrence of such hydrogen bonds has been shown to be important in enhancing the formation of octahedral environments around transition–metal ions in so far as pyrazole complexes are concerned.[7,9,26]

The electronic spectrum of $[CuCl_2(pdmp)_2]$ is quite different from that of $[Cu(NO_3)_2(pdmp)_2]$; in this last named complex the copper atom is surrounded by two nitrogen atoms (from the pyrazole rings) and two oxygen atoms (from the nitrate groups) in a near square-planar environment, with a *cis* geometry.[6] The N–Cu–N, O–Cu–O and the two O–Cu–N angles are 96.6, 84.3, 88.8 and 90.3°, respectively. Its spectrum (in nitromethane solution) presents a *single* broad and asymmetrical absorption band with maximum at 15.0 kK ($\epsilon = 49\ M^{-1}.cm^{-1}$). The magnetic moment (2.0 ± 0.1 B.M.) and the mentioned spectral behaviour would be more consistent with a tetragonally distorted six-coordinate complex.[7,20,21,27,28] However, it is important to mention that in this complex one oxygen atom of each planar NO_3^- group is coordinated to the Cu(II) ion (Cu–O bond lengths of 2.016 and 2.039 Å) and each NO_3^- has also another oxygen close to the Cu(II) ion (Cu–O distances of 2.494 and 2.473 Å; the concerned O–Cu–O angle is 123.4°) completing a very distorted octahedron.[6] So, there is no conflict among the spectral, magnetic and structural data determined for the complex under consideration. On the other hand, the spectral differences observed for the chloride and nitrate complexes seem fully justified as they in fact exhibit distinct configurations.

The values found for the magnetic moments of these complexes suggest that bridged polymeric structures and/or strong Cu–Cu interactions should be absent.[8,21] Also, it has been found that copper(II) complexes to which distorted square-planar or octahedral structures have been assigned present magnetic moments slightly but consistently higher than those displayed by the regular square-planar complexes.[21,27,28] These conclusions are in line with the ones drawn from the X-ray investigations reported herein and elsewhere.[6]

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REFERENCES

1. M. Molina and S. Tabak, *J. Inorg. Nucl. Chem.*, **34**, 2985 (1972).
2. A. C. Massabni, M. Molina, C. Melios, M. P. Dalponte and N. M. P. Moraes, *Proc. XII Congr.* Latinoamericano de Química, Quito (Ecuador), 1976, p. 49.
3. C. Melios, M. Molina, H. Yamanaka and J. O. Tognolli, *Proc. IV Int. Symp.* Solute–Solute–Solvent Interactions, Vienna, 1978, pp. 208–210.
4. M. P. D. Mattioli, A. C. Massabni, C. B. Melios and M. Molina, in preparation.
5. R. H. P. Francisco, Y. P. Mascarenhas and J. R. Lechat, *Acta Cryst.* **B35**, 177 (1979).
6. R. H. P. Francisco, J. R. Lechat and Y. P. Mascarenhas, *Acta Cryst.* **B35**, 1468 (1979).
7. J. Reedijk, *Rec. Trav. Chim.*, **89**, 605, 993 (1970).

8. D. Nicholls and B. A. Warburton, *J. Inorg. Nucl. Chem.*, **33**, 1041 (1971).
9. J. Reedijk, J. C. A. Windhorst, N. H. M. Van Ham and W. L. Groeneveld, *Rec. Trav. Chim.*, 90, 234 (1971).
10. B. K. S. Lundberg, *Acta Chem. Scand.*, **26**, 3977 (1972).
11. V. M. Agre, I. A. Krol and V. K. Trunov, *Dokl. Akad. Nauk. SSSR*, **232**, 341 (1977).
12. B. N. Figgis and J. Lewis, in "Modern Coordination Chemistry", (J. Lewis and R. G. Wilkins, Eds.), Interscience, N. York, 1960, p. 403.
13. G. Germain, P. Main and M. M. Woolfson, *Acta Cryst.*, **A27**, 368 (1971).
14. "International Tables for X-Ray Crystallography", vol. IV, Kynoch Press, Birmingham, England, 1974.
15. C. K. Johnson, ORTEP, Report No. ORNL – 3794, Oak Ridge National Laboratory, Oak Ridge, Tenn. (1965).
16. D. C. Mente and R. J. Sundberg, *Inorg. Chim. Acta*, **26**, 271 (1978).
17. V. F. Duckworth and N. C. Stephenson, *Acta Cryst.*, **B25**, 1795 (1969).
18. M. Laing and G. Carr, *J. Chem. Soc. (A)*, 1141 (1971).
19. M. J. Bagley, D. Nicholls and B. A. Warburton, *J. Chem. Soc. (A)*, 2694 (1970).
20. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1968, pp. 355–359.
21. M. Akbar Ali and S. G. Teoh, *J. Inorg. Nucl. Chem.*, **40**, 451 (1978) and references quoted therein.
22. Y. Nishida and S. Kida, *Coord. Chem. Rev.*, 27, 275 (1979).
23. W. E. Hatfield and R. Whyman in "Transition Metal Chemistry", (R. L. Carlin, Ed.), vol 5, M. Dekker, N. York, 1969, p. 53.
24. R. J. Sundberg and R. B. Martin, *Chem. Rev.*, 74, 471 (1974).
25. J. D. Dunitz, *Acta Cryst.*, 10, 307 (1957).
26. A. Mighell, A. Santoro, E. Prince and C. Reimann, *Acta Cryst.*, **B31**, 2479 (1975) and references quoted therein.
27. R. V. Biagetti, W. G. Bottjer and H. M. Haendler, *Inorg. Chem.*, 5, 379 (1966).
28. S. N. Poddar and S. R. Chowdhury, *Indian J. Chem.*, **12**, 1107 (1974).