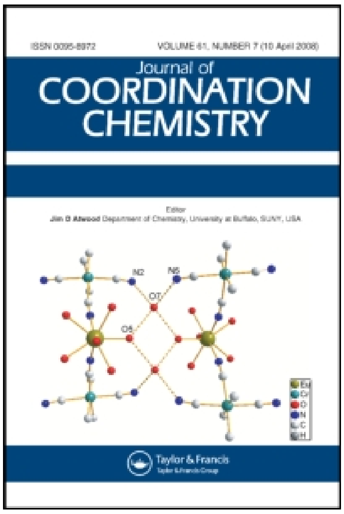

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REACTIONS OF DI(1-PYRAZOLYL)PROPANE-COPPER(II) COMPLEXES WITH VARIOUS ANIONS

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The reactivity of some di(1-pyrazolyl)propanecopper (II) complexes with various anions in aqueous solutions has been studied. Di(1-pyrazolyl)propanecopper (II) chloride, $Cu(Me_2Cpz_2)Cl_2$, reacts readily with pseudohalide ions to give complexes of the type, $Cu(Me_2Cpz_2)Z_2$ ($Z = SCN^-, NCO^-, N_3^-$). With PF_6^- and BPh_4^- anions, complexes of the type $[Cu(Me_2Cpz_2)_2X]Y$ ($Y = PF_6^-$, $X = Cl^-$, Br^- and NO_3^-; $Y = BPh_4^-$, $X = Cl^-$) are formed. However, the reaction of $Cu(Me_2Cpz_2)Cl_2$ with acetylacetonate (acac), dialkyldithiocarbamate (S_2CNMe_2, S_2CNEt_2), or poly(1-pyrazolyl)borate ($H_2BPz_2^-$, $HBpz_3^-$) anions leads to the displacement of Me_2CPz_2 and the subsequent formation of neutral $Cu(acac)_2$, $Cu(S_2CNR_2)_2$, $Cu(H_2Bpz_2)_2$ and $Cu(HBpz_3)_2$ complexes. Reaction products have been characterised by elemental analysis, magnetic moments and infrared spectral measurements.

INTRODUCTION

Several complexes of transition metal salts with poly(1-pyrazolyl)alkane ligands have been isolated and characterised.[1-9] In one case, the structure of the complex ($Ni(LL)_2Cl_2$, LL = di(3,5-pyrazolyl)methane) has been determined by x-ray diffraction.[6] The chemical reactions of these complexes have not been investigated. This lack of information as well as the fact that some of the complexes are potential starting materials for the synthesis of a variety of mixed chelates prompted us to investigate the chemical reactivity of $Cu(Me_2Cpz_2)Cl_2$ with various anions. It was thought that mixed chelates would be formed with the bidentate anions.

EXPERIMENTAL

Chemicals

All the chemicals, with the exception of the Me_2Cpz_2 ligand, were obtained commercially and used without any further purification. Me_2Cpz_2 was prepared from pyrazole and 2,2-dimethoxypropane according to Trofimenko's procedure.[8]

Preparation of $Cu(Me_2Cpz_2)Cl_2$

$CuCl_2.2H_2O$ (5.0g, 0.029 mol) dissolved in about 20 cm^3 methanol was added with stirring to about 20 cm^3 of a methanolic solution of Me_2Cpz_2 (5.17g, 0.029 mol). The mixture gave an immediate green precipitate. This was filtered under suction, washed several times with methanol and dried in a vacuum oven at 45°.

Reactions of the complex with various anions

All the reactions were carried out in aqueous solution. $Cu(Me_2Cpz_2)Cl_2$ dissolved in minimum quantity of water was added to the appropriate equimolar quantity of the sodium salt of the anion dissolved in the minimum quantity of the same solvent. An immediate precipitate resulted in each case. The precipitate was filtered under suction, washed several times with water and dried in a vacuum oven at 45°. In the case of PF_6^- reactions, the reaction mixture had to be stirred to initiate crystallization of the product. Analytical data are given in Table I.

Physical measurements

The melting points were determined on an electrochemical melting point apparatus. The microanalyses were performed by the staff of University College, London. The electronic absorption spectral measurements in acetone solutions were carried out using a Pye Unicam SP8 - 150 spectrophotometer. The i.r. spectra were recorded in nujol mulls between CsI plates on a Pye Unicam Sp 2000 spectrophotomer.

The magnetic susceptibilities were measured at room temperature by the Guoy method using $HgCo(NCS)_4$ as calibrant and correcting for diamagnetism with the appropriate Pascal constants.

RESULTS AND DISCUSSION

$Cu(Me_2Cpz_2)Cl_2$

Di(1-pyrazolyl)propane, Me_2Cpz_2, reacts with copper(II) chloride to give a stable 1:1 complex. No 1:2 complex could be obtained even with the use of a large excess of the ligand. This behaviour contrasts with that of di(3,5-dimethylpyrazolyl)methane which forms both 1:1 and 1:2 complexes with $CuCl_2$ and $CuBr_2$ depending upon the metal: ligand ratio used.[5] The complex is soluble in water but only sparingly soluble in the common organic solvents. Therefore, all the reactions were carried out in aqueous solutions.

Reactions with pseudohalide anions

$Cu(Me_2Cpz_2)Cl_2$ reacts with pseudohalides to give immediate precipitates from aqueous solution. The analytical and physical data for these newly prepared complexes are listed

TABLE I
Physical and Analytical Data for the Complexes.

Complex	Colour	M.P. (°)	Analysis found (Calc) %		
			C	H	N
$Cu(Me_2Cpz_2)Cl_2$	olive green	200 – 202	34.85 (34.80)	3.90 (3.89)	18.13 (18.03)
$Cu(Me_2Cpz_2)(SCN)_2$	dark green	134 – 136	37.06 (37.11)	3.62 (3.40)	23.70 (23.61)
$Cu(Me_2Cpz_2)(CNO)_2$	blue	202 – 204	40.55 (40.80)	3.92 (3.74)	25.81 (25.96)
$Cu(Me_2Cpz_2)(N_3)_2$	dark green	191 – 192	33.41 (33.38)	3.71 (3.74)	42.94 (43.26)
$[Cu(Me_2Cpz_2)_2Cl]BPh_4$	greenish yellow	110 – 112	65.07 (65.45)	5.67 (5.77)	14.34 (14.54)
$[Cu(Me_2Cpz_2)_2Cl]PF_6$	blue	174 – 176	36.10 (36.25)	4.01 (4.06)	18.77 (18.79)
$[Cu(Me_2Cpz_2)_2Br]PF_6$	deep green	178 – 180	33.64 (33.50)	3.75 (3.75)	17.56 (17.30)
$[Cu(Me_2Cpz_2)_2NO_3]PF_6$	blue	175 – 178	34.65 (34.70)	3.92 (3.89)	20.30 (20.24)

in Table I. Attempts to prepare mixed halide-pseudohalide complexes by using a $Cu(Me_2Cpz_2)Cl_2$: pseudohalide ratio of 1:1 were unsuccessful. The reaction between $Cu(Me_2Cpz_2)Cl_2$ and KCN did not give an analytically pure product despite the fact that it had a sharp melting point at 167-169°. However, the disappearance of the ν_{Cu-Cl} band and the simultaneous appearance of a new band at 2100 cm^{-1} with a shoulder at 2130 cm^{-1} assignable to ν_{CN} vibrations in the product can be taken as an evidence of the displacement of the chloride ions by cyanide ions. In contrast to the starting complex, $Cu(Me_2Cpz_2)Cl_2$, the pseudohalide complexes are insoluble in water. However, they are partially soluble to varying degrees in the common organic solvents.

The data in Table II show that the i.r. spectra of all the complexes have bands of medium to strong intensity in the region 371–400 cm^{-1} which are not present in the infrared spectrum of the pure ligand. These bands are attributed predominantly to ν_{Cu-N} vibrations.[10–12] This provides evidence for the coordination of the ligand to the Cu^{2+} ion *via* the pyrazolyl nitrogen atoms. Present in the i.r. spectra of all the complexes are medium to strong bands between 599 and 625 cm^{-1} (not shown in the Table) assignable to pyrazoly ring deformation modes.[10,11]

The i.r. spectrum of $Cu(Me_2Cpz_2)Cl_2$ exhibits two strong bands at 295 and 280 cm^{-1} which are assigned to terminal ν_{Cu-Cl} vibrations. This is indicative of a four coordinate pseudo-tetrahedral structure.[3] The magnetic moment of the complex (1.94 B.M.) is within the range of values expected for monomeric copper(II) complexes.[13]

The i.r. spectra of the pseudohalide complexes have sharp bands characteristic of pseudohalide ions in the region 2040-2250 cm^{-1}. Their band positions shown in Table II indicate the absence of bridging pseudohalide ions. This view is further supported by the fact that all the complexes have the normal magnetic moments (Table 2) expected for monomeric copper(II) complexes. The visible absorption bands observed at 646 and 644 nm for the SCN^- and NCO^- complexes assignable to d-d transitions are indicative of a square-planar structure. The azido complex was insufficiently soluble for the d-d band to be measured in solution. It is however assumed that it too has a similar square planar structure.

Reactions with PF_6^- and BPh_4^- anions

The reactions of PF_6^- and BPh_4^- anions with $Cu(Me_2Cpz_2)Cl_2$ afforded $[Cu(Me_2Cpz_2)_2Cl]Y$ ($Y = PF_6^-, BPh_4^-$). The reactions probably occurred by disproportionation according to the following equation.

$$2Cu(Me_2Cpz_2)Cl_2 + NH_4PF_6 \rightarrow [Cu(Me_2Cpz_2)_2Cl]PF_6 + CuCl_2 + NH_4Cl.$$

Although a similar complex has been obtained with other poly(1-pyrazolyl)alkanes,[1,2,4] it has not been previously obtained directly by reacting the transition metal complex of the poly(1-pyrazolyl)alkane with the polyanion. The usual procedure is to add slightly more than stoichiometric amount of the polyanion dissolved in methanol to a hot solution of the metal salt and the ligand in the same solvent. This procedure was tested using copper(II) chloride and bromide as the metal salts. The reactions can be represented by the following equation

$$CuX_2.nH_2O + 2Me_2Cpz_2 + NH_4PF_6 \rightarrow [Cu(Me_2Cpz_2)_2X]PF_6 + 2NH_4Cl + nH_2O.$$

$$(X = Cl, n = 2; Br, n = 0).$$

The $[Cu(Me_2Cpz_2)Cl]PF_6$ complex obtained from this reaction is identical with the one produced by the method outlined above.

TABLE II
Magnetic Moments, Electronic and Important Infrared Spectral Data.

Complex	Visible Spectra[a] λ_{max} (nm)		Infrared spectra cm^{-1}		U_{eff} (B.M) at 25°
	d-d band	CT band	Anion bands	$\nu_{\text{Cu-N}}$	
$Cu(Me_2Cpz_2)Cl_2$	730	424	295 280 vs, $\nu_{\text{Cu-Cl}}$	390 375 m	1.94
$Cu(Me_2Cpz_2)(SCN)_2$	646	416	2132 2100 vs, ν_{CN}; 668m, ν_{CS}; 468m, δ_{NCS}	387 w	1.75
$Cu(Me_2Cpz_2)(NCO)_2$	726sh, 644	352sh, 332	2224 vs, ν_{aNCO}; 620m, δ_{NCO}; 348 vs, $\nu_{\text{Cu-NCO}}$	380 m	1.86
			1335 1324 s, ν_{sNCO}		
$Cu(Me_2Cpz_2)(N_3)_2$	b	400	2040 vs, $\nu_{aN_3^-}$; 1285 1273 s, $\nu_{sN_3^-}$;	382 s	1.94
			351 340 s, $\nu_{\text{Cu-N}_3}$		
$[Cu(Me_2Cpz_2)_2Cl]BPh_4$	b		1580, ν_{CC}; 292m, $\nu_{\text{Cu-Cl}}$	380m	2.03
$[Cu(Me_2Cpz_2)_2Cl]PF_6$	850sh, 741	330	860 839 vs, ν_3 PF_6^-; 285vs, $\nu_{\text{Cu-Cl}}$	390 378 s	2.13
$[Cu(Me_2Cpz_2)_2Br]PF_6$	748, 550sh	342	860 835 vs, ν_3 PF_6^-; 245 s, $\nu_{\text{Cu-Br}}$	390 378 s	1.65
$[Cu(Me_2Cpz_2)_2NO_3]PF_6$	710	328	1780 1750 w $\nu_1 + \nu_4$; NO_3^-; 1315 1295 s, ν_1 NO_3^-;	382s	2.01
			830vs, ν_3 PF_6^-		

[a]In acetone solution. [b]Insufficiently soluble for spectral measurements.

Attempts to prepare $[Cu(Me_2CPz_2)_2](PF_6)_2$ by using NH_4PF_6 in large excess were unsuccessful; the product was always $[Cu(Me_2Cpz_2)_2X]PF_6$ (X = Cl, Br). The failure was thought to be due to the strong bonding of the halide ion in $[Cu(Me_2Cpz_2)_2X]Y$ to the Cu^{2+} ion. Thus the reactions were repeated using copper(II) nitrate with the hope that both nitrate ions, being more weakly coordinating than the halogen ions, would be replaced. Again, the result as confirmed by the microanalytical and i.r. spectral data, was the isolation of $[Cu(Me_2Cpz_2)_2NO_3]PF_6$. These results would seem to suggest that the structure of the complex ion is perhaps the more crucial factor than the Cu-anion bond strength. Thus the failure to obtain $[Cu(Me_2Cpz_2)_2](PF_6)_2$ has been interpreted to imply that the square pyramidal structure (*I*) is more stable than the square planar structure (*II*).

In addition to the common i.r. features of the complexes already discussed, the i.r. spectra of $[Cu(Me_2Cpz_2)_2X]Y$ (X = Cl, Br and NO_3, Y = PF_6) show broad bands at *ca* 830 - 860 cm^{-1} assignable to $\nu_{3\,PF_6^-}$ vibrations. This observation is consistent with ionic hexafluorophosphate being present. The appearance of two strong bands at 285 and 245 cm^{-1} assignable to terminal ν_{Cu-Cl} and ν_{Cu-Br} vibrations respectively in the i.r. spectra of $[Cu(Me_2Cpz_2)_2X]PF_6$ (X = Cl, Br) rule out any halide bridged structure in these complexes. A monomeric five coordinate structure is therefore suggested for the $[Cu(Me_2Cpz_2)_2X]^+$ complex ion. The magnetic moment and electronic spectral data (Table II) support this view.

The i.r. spectrum of $[Cu(Me_2Cpz_2)_2Cl]BPh_4$ is quite distinct from the others in the regions 1100-1050 cm^{-1} and 800-700 cm^{-1}. No attemps has been made to assign the bands in these regions due to the complex nature of the spectrum. However, most of the bands are associated with phenyl group vibrations. A medium band at 292 cm^{-1} is probably the terminal $\nu_{(Cu-Cl)}$ vibration. The magnetic moment of 2.03 B.M. is consistent with a monomeric structure. Therefore, a square pyramidal copper(II) complex ion with the chloride ion occupying an axial position is proposed.

For the complex $[Cu(Me_2Cpz_2)_2NO_3]PF_5$, it is difficult to assign with certainty the bands associated with NO_3 stretching vibrations due to overlap with nujol and ligand bands. However, the i.r. spectrum shows two weak bands at 1750 and 1780 cm^{-1} assignable to ($\nu_1 + \nu_4$; NO_3^-) combination bands. Since only two bands with a separation of 40 cm^{-1} are observed in this region, the nitrate is considered to be coordinated as a bidentate.[14]

Reactions with bidentate anions

The reactions of $Cu(Me_2Cpz_2)Cl_2$ with the potentially bidentate anions acetylacetonate ($acac^-$), dialkyldithiocarbamate ($S_2CNR_2^-$; R = CH_3, C_2H_5), di(1-pyrazolyl)borate ($H_2BPz_2^-$), and tri(1-pyrazolyl)borate ($HBpz_3^-$) were investigated with the expectation of five-or six-coordinate mixed chelates by using appropriate complex: anion mol ratios. The properties and spectral data of the reaction products clearly indicate that the reactions instead led to the displacement of the Me_2Cpz_2 ligand. The reaction products analysed as $Cu(acac)_2$, $Cu(S_2CNR_2)_2$, $Cu(H_2Bpz_2)_2$ and $Cu(HBpz_3)_2$. These reactions seem to support the view that $Cu(Me_2Cpz_2)Cl_2$ might exist as the hydrated $[Cu(Me_2Cpz_2)]^{2+}$ ion in aqueous solution. The displacement of the Me_2Cpz_2 ligand is probably favoured because of the high stability and the insolubility of the neutral reaction products. It will be recalled that precipitates always formed instantaneously on mixing the aqueous solutions of $Cu(Me_2Cpz_2)Cl_2$ and the anion.

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