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COMMUNICATION

Self-assembly of a supramolecular oligomer containing three different cobalt(II) environments; the first structurally characterised polymer derived from 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz)

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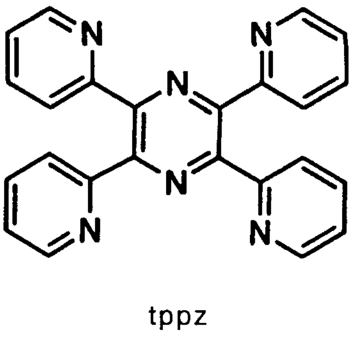
The reaction of cobalt(II) chloride with 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) in the presence of sodium chloride gives polynuclear complexes; recrystallisation from acetonitrile yields a linear polymer containing three different types of cobalt(II) environment. This compound, $[\{(\mu\text{-Cl})_2(\text{MeCN})\text{Co(tppz)Co(CoCl}_4)\}_n]$, has been structurally characterised (orthorhombic, $P2_12_12_1$, a = 12.967(3), b = 14.624(3), c = 18.043(4) Å, V = 3421.5(13) Å^3, Z = 4, R_1 = 0.0584, wR_2 = 0.1868).

There is considerable current interest in the assembly of supramolecular oligomers and polymers by the use of multinucleating ligands containing two or more 2,2':6',2"-terpyridine (tpy) domains.[1] Recently, we have become interested in 2,3,5,6-tetra(2-pyridyl)pyrazine (tppz) which is the prototype for a species with two tpy domains. Although early reports suggested that tppz only behaved as a mononucleating tridentate ligand,[2] the bridging mode is now well-established.[3] To date only the tridentate mode has been described for cobalt(II) complexes of tppz[2,5], although dinuclear cobaltiron and cobaltruthenium species have been mentioned in passing. Supramolecular species containing tppz are currently attracting interest,[6] in this communication we describe a novel cobalt(II) complex of tppz.

The reaction of tppz with cobalt(II) chloride in EtOH or MeOH in a 2:1 ratio gives only $[\text{Co(tppz)}_2]^{2+}$[7]; we have confirmed the nature of this complex by solution NMR studies and by a crystallographic study of the hexafluorophosphate salt.[8] However, when the ratio of cobalt(II) chloride to tppz varies in the range 2:1 to 3.5:1, a variety of new green or brown products is obtained. Analytical and spectroscopic data suggested that these complexes contained $[\text{CoCl}_4]^{2-}$ ions, and we considered that the addition of excess chloride to the reaction mixture might allow the isolation of pure products. Mixing methanolic tppz with an ethanolic solution of sodium chloride and cobalt(II) chloride (1:8.3:2.25 molar ratios) gives a red-brown solution. Evaporation of the



tppz

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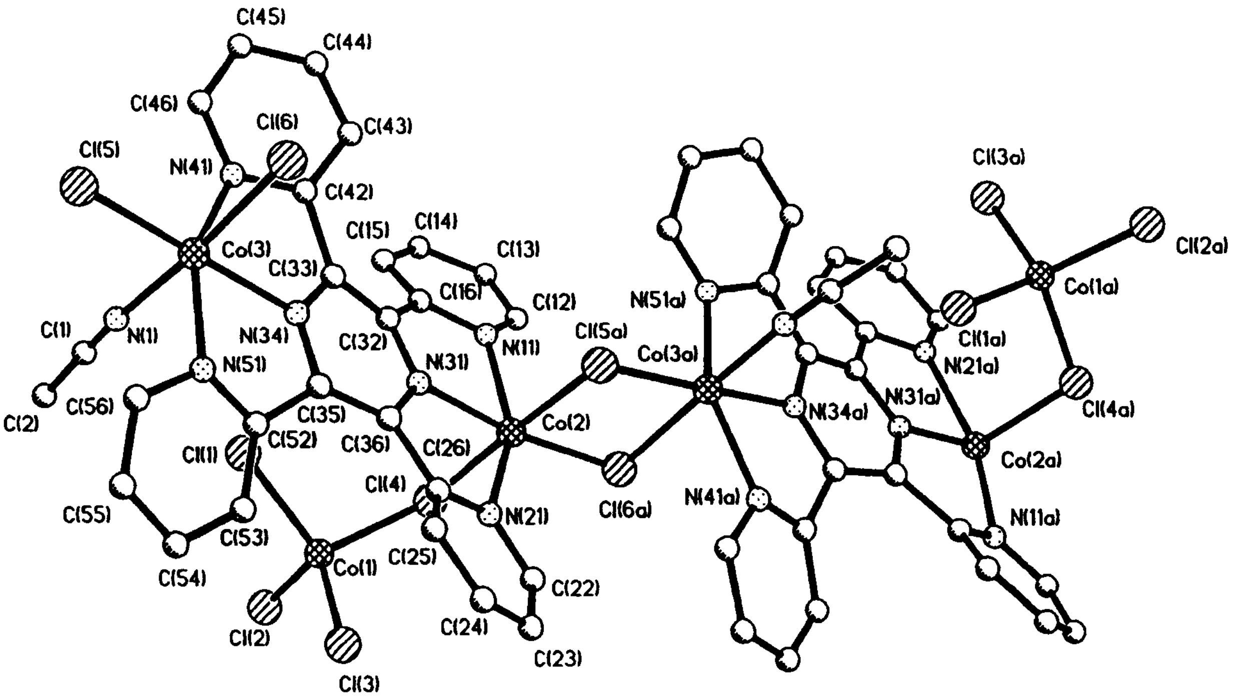

Figure 1 The crystal and molecular structure of [{(μ-Cl)$_2$(MeCN)Co(tppz)Co(CoCl$_4$)}$_n$} showing the numbering scheme adopted. Two of the formula units present in the polymer are shown in this representation.

solvent, followed by recrystallisation from acetonitrile gave large green crystals of a cobalt(II) compound formulated {Co$_3$Cl$_6$(MeCN)(tppz)} in 52% yield. The same product was obtained by recrystallisation from acetonitrile of the green solid obtained from the reaction of tppz with cobalt(II) chloride in acetonitrile.[9]

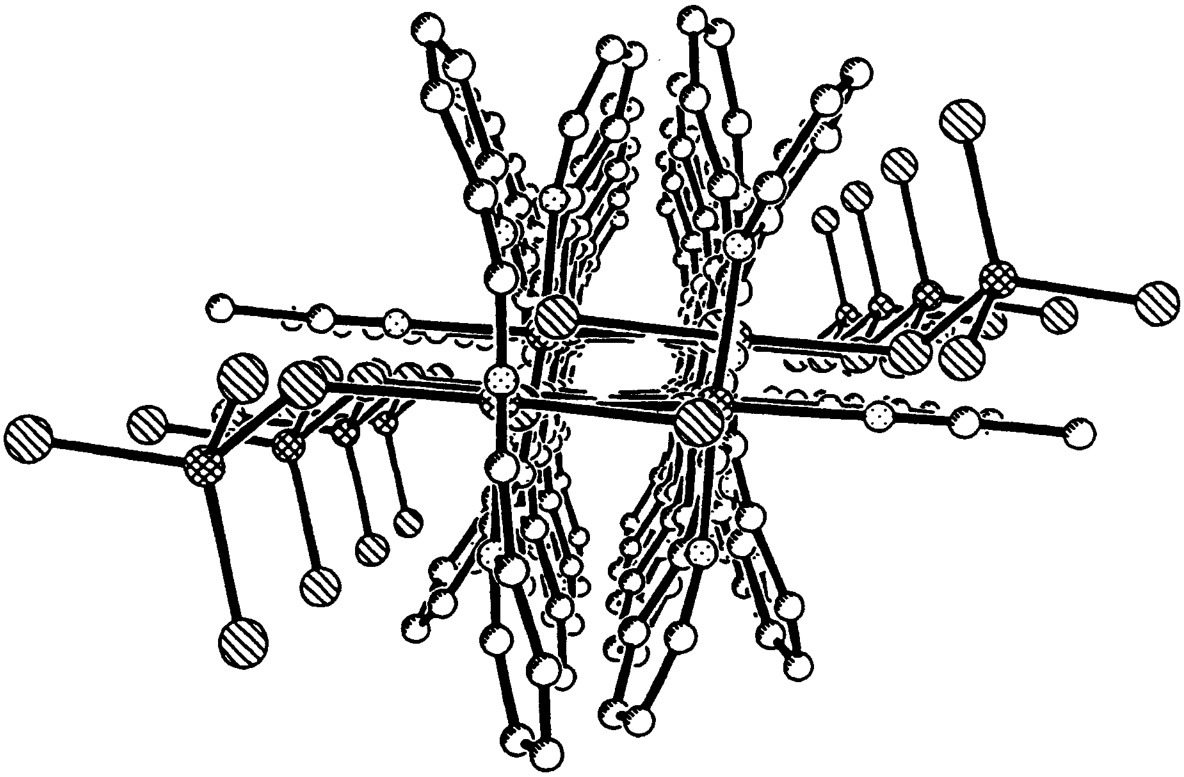

Figure 2 A view along the polymer [{(μ-Cl)$_2$(MeCN)Co(tppz)Co(CoCl$_4$)}$_n$] showing the 'box-like' structure.

We have determined the crystal structure of this material,[10] and shown it to be an infinite polymer containing three different cobalt(II) environments; a view of the polymer presented in Fig. 1. Two six-coordinate cobalt centres are utilised in the formation of a linear "box-like" polymer (Fig. 2). Each of the six coordinate cobalt centres is coordinated to a tridentate domain from a tppz ligand and they are bridged by two chloride ligands. The coordination sphere of cobalt(2) is completed by a tetrahedral $CoCl_4$ ligand whilst that of cobalt(3) is completed by an acetonitrile. The terminal pyridine rings of each tppz ligand are considerably ruffled, but the two tridentate domains of each are approximately coplanar. The chloride bridging between Co(2) and Co(3a) leads to an alternate up-down arrangement of the planes of adjacent tppz ligand (Fig. 2). The Co-N and Co-Cl distances are all typical, as are the intraligand bonding parameters. The intermetallic distances are Co(3)...Co(2), 6.852 Å, Co(2)...Co(3a), 3.531 Å and Co(1)...Co(2), 4.092 Å.

The complex is paramagnetic in the solid state, and possesses a magnetic moment per formula unit (three cobalt atoms) varying between 8.0 and 8.3 BM over the temperature range 100K to 300K (SQUID, 3.0 Tesla applied field). Over this temperature range Curie-Weiss behaviour was observed. This is consistent with the presence of two high-spin octahedral and one tetrahedral cobalt(II) centre.[13]

Upon dissolution in acetonitrile, $[(MeCN)Cl_2Co(tppz)CoCl_2(MeCN)]$ and related oligomeric complexes are formed. However, concentration of these acetonitrile solutions regenerates the solid state polymeric material. We are currently investigating the nature of these solution species and the conducting a systematic study of the assembly of such solid state materials with a variety of metal ions and multinucleating ligands.

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REFERENCES

1 See for example: Constable, E.C.; Edwards, A.J.; Marcos, M.D.; Martínez-Máñez, R.; Raithby, P.R.; Tendero, M.J.L.; *Inorg. Chim. Acta* **1994**, *224*, 11; Constable, E.C.; Cargill Thompson, A.M.W.; *J. Chem. Soc., Dalton Trans.* **1994**, 1409; Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E.C.; Cargill Thompson, A.M.W.; *Coord. Chem. Rev.* **1994**, *132*, 209; Newkome, G.R.; Cardullo, F.; Constable, E.C.; Moorefield, C.N.; Cargill Thompson, A.M.W.; *J. Chem. Soc., Chem. Commun.* **1993**, 925; Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E.C.; Cargill Thompson, A.M.W.; *J. Chem. Soc., Chem. Commun.* **1993**, 942; Constable, E.C.; Cargill Thompson, A.M.W.; Tocher, D.A.; *Makromol. Symp.* **1994**, *77*, 219; Barigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.-P.; Sauvage, J.-P.; Sour, A.; Constable, E.C.; Cargill Thompson, A.M.W.; *J. Am. Chem. Soc.*, **1994**, *116*, 7692.

2 Goodwin, H.A.; Lions, F.; *J. Am. Chem. Soc.* **1959**, *81*, 6415; Goodwin, H.A.; Sylva, R.N.; Vagg, R.S.; Watton, E.C.; *Aust. J. Chem.* **1969**, *22*, 1605.

3 See for example: Arana, C.R.; Abruña, H.D.; *Inorg. Chem.* **1993**, *32*, 898; Vogler, L.M.; Scott, B.; Brewer, K.J.; *Inorg. Chem.* **1993**, *32*, 898; Graf, M.; Greaves, B.; Stoeckli-Evans, H.; *Inorg. Chim. Acta* **1993**, *204*, 239; Tummel, R.P.; Chirnyil, S.; *Inorg. Chim. Acta* **1989**, *154*, 77; Ruminski, R.R.; Kipling, T.; Cockroft, T.; Chase, C.; *Inorg. Chem.* **1989**, *28*, 370.

4 Petersen, J.D.; Morgan, L.W.; Hsu, I.; Billadeau, M.A.; Ronco, S.E.; *Coord. Chem. Rev.* **1991**, *111*, 319.

5 Okamoto, Y.; Ogura, K.; Kinoshita, T.; *Polyhedron* **1984**, *3*, 635.

6 Graf, M.; Stoeckli-Evans, H.; *Acta Crystallogr., Sect. C* **1994**, *C50*, 1461.

7 $[Co(tppz)_2][PF_6]_2$, orange solid, Found: C, 50.4; H, 2.9; N, 14.9% Calcd. for $C_{48}H_{32}N_{12}CoP_2F_{12}$: C, 51.2; H, 2.9; N, 14.9%; FAB MS, *m/z* 981 ($[Co(tppz)_2][PF_6]$), 836 ($[Co(tppz)]$), 447; $E_{1/2}$ Co(II)/Co(III), 0.064 V *vs* Fc/.Fc$^+$.

8 Constable, E.C.; Phillips, D.; Raithby, P.R.; Unpublished results.

9 In a typical preparation, tppz (40 mg, 0.103 mmol) was added to a solution of $CoCl_2•6H_2O$ (73.5 mg, 0.31 mmol) in acetonitrile (30 cm^3). After 30 minutes of stirring at room temperature the green precipitate was collected by filtration and recrystallised from acetonitrile to give $\{Co_3Cl_6(MeCN)(tppz)\}$ as large green crystals (66 mg).

10 *Crystal data*: $C_{26}H_{19}Cl_6Co_3N_7$, green crystals, $M = 818.97$, orthorhombic, space group $P2_12_12_1$, $a = 12.967(3)$, $b = 14.624(3)$, $c = 18.043(4)$ Å, $\alpha = \beta = \gamma = 90°$, $U = 3421.5(13)$ Å^3, $Z = 4$, $D_c = 1.590$ g cm^{-1}, $F(000) = 1628$, Mo-Kα radiation ($\lambda = 0.71073$ Å), μ(Mo-Kα) = 7.82 cm^{-1}. 5039 Reflections were collected on a STOE four circle diffractometer with 2θ(max) 45.0° of which 4456 were unique and were used in structure solution using SHELXTL PLUS[11] and refined using SHELX-93[12] (Co, Cl, N, C anisotropic) to $R1 = 0.0584$ [$F > 4\sigma(F)$, for 4177 reflections], $wR2 = 0.0732$ (all data). The largest peak and largest hole in the final difference map were 3.247 and -1.178 eÅ^{-3} respectively. The large residual of 3.247 eÅ^{-3} is located close to one of the cobalt atoms, but could not be modelled.

11 SHELXTL PLUS, Program version 4.0, Siemens Analytical X-Ray Instruments, Madison, WI, **1990.**

12 Sheldrick, G.M.; SHELX 93, University of Gottingen, **1993.**

13 Variable temperature magnetic susceptibility measurements were made using a Quantum Design SQUID magnetometer. Measurements were made under an applied field of 3.0T. The sample was cooled to 6 K in zero field prior to measurement of the magnetisation. The temperature was then raised in increments of either 2.5 K or 5.0 K until an upper limit of 300 K was reached. The data were fitted by $\chi_m = \chi_0 + C_m/(T - \theta)$ where χ_0 allows for a Van Vleck component.