were included in calculated positions and refined using a riding model, including free rotation about X—CH_3 bonds, and with $U_{iso}(H) = 1.2U_{eq}(X)$ ($1.5U_{eq}$ for methyl H atoms).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXL*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *Xtal*3.4 (Hall *et al.*, 1995). Software used to prepare material for publication: *Xtal*3.4.

The authors wish to thank Professor P. H. van Rooyen of the Department of Chemistry of the University of Pretoria, South Africa, for collecting the diffraction data.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1218). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Beak, P. & Lee, W. K. (1993). *J. Org. Chem.* **58**, 1109–1117.

Das, V. G. K., Mun, L. K., Wei, C., Blunden, S. J. & Mak, T. C. W. (1987). *J. Organomet. Chem.* **322**, 163–175.

Das, V. G. K., Mun, L. K., Wei, C. & Mak, T. C. W. (1987). *Organometallics*, **6**, 10–14.

Doidge-Harrison, S. M. S. V., Nowell, I. W., Cox, P. J., Howie, R. A., Taylor, O. J. & Wardell, J. L. (1991). *J. Organomet. Chem.* **401**, 273–282.

Dräger, M. (1983). *J. Organomet. Chem.* **251**, 209–214.

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Farina, V. (1996). *Pure Appl. Chem.* **68**, 73–78.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Fu, F., Li, H., Zhi, D., Fang, Q., Pan, H., Tiekink, E. R. T., Kayser, F., Biesemans, M., Verbruggen, I., Willem, R. & Gielen, M. (1995). *J. Organomet. Chem.* **490**, 163–171.

Godard, A., Rocca, P., Fourquez, J., Rovera, J. & Marsais, F. (1993). *Tetrahedron Lett.* **34**, 7919–7922.

Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). Editors. *Xtal*3.4 *Reference Manual*. University of Western Australia, Australia.

Jastrzebski, J. T. B. H., Boersma, J., Esch, P. M. & van Koten, G. (1991). *Organometallics*, **10**, 930–935.

Jousseaume, B., Villeneuve, P., Drager, M., Roller, S. & Chezeau, J. M. (1988). *J. Organomet. Chem.* **349**, C1–C3.

Jurkschat, K., Tzschach, A. & Meunier-Piret, J. (1986). *J. Organomet. Chem.* **315**, 45–49.

Kayser, F., Biesemans, M., Delmotte, A., Verbruggen, I., De Borger, I., Gielen, M. & Willem, R. (1994). *Organometallics*, **13**, 4026–4032.

Lorberth, J., Shin, S.-H., Donath, H. & Wocadlo, S. (1991). *J. Organomet. Chem.* **407**, 167–171.

Molina, P., Murica, F. & Fresneda, P. M. (1994). *Tetrahedron Lett.* **35**, 1453–1456.

Murakami, M., Yoshida, T., Kawanami, S. & Ito, Y. (1995). *J. Am. Chem. Soc.* **117**, 6408–6409.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Pearson, W. H., Lindbeck, A. C. & Kampf, J. W. (1993). *J. Am. Chem. Soc.* **115**, 2622–2636.

Selvaratnam, S., Lo, K. M. & Das, V. G. K. (1994). *J. Organomet. Chem.* **464**, 143–148.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Turner, J. A. (1983). *J. Org. Chem.* **48**, 3401–3408.

Veith, M., Zimmer, M., Huch, V., Denat, F., Gaspard-Iloughmane, H. & Dubac, J. (1993). *Organometallics*, **12**, 1012–1015.

Acta Cryst. (1998). C**54**, 762–764

trans-Diaquadichlorobis(6-methyl-2-pyridone-*O*)cobalt(II) Bis(6-methyl-2-pyridone) Solvate

Colin Buchanan, Simon Parsons and Richard E. P. Winpenny

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland. E-mail: s.parsons@ed.ac.uk

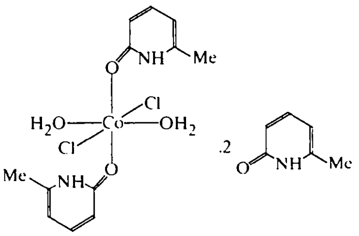
(*Received 8 August 1997; accepted 7 January 1998*)

Abstract

The crystal structure of the title compound, $[CoCl_2(C_6H_7NO)_2(H_2O)_2].2C_6H_7NO$, consists of a one-dimensional hydrogen-bonded polymer in which $[CoCl_2(Hmhp)_2(H_2O)_2]$ complexes alternate with pairs of unbound Hmhp molecules (Hmhp = 6-methyl-2-pyridone).

Comment

We have recently reviewed the extensive structural chemistry of complexes of the late first row transition metals with 6-substituted pyridonate ligands (Parsons & Winpenny, 1997). The immense structural diversity of these systems can be illustrated by reference to cobalt, which forms complexes ranging from one-dimensional polymers (Blake *et al.*, 1998) to one in which a fragment of $Co(OH)_2$ containing 24 Co centres is encapsulated by 6-methyl-2-pyridonate (mhp), OH and Cl ligands (Brechin *et al.*, 1997). We now report the crystal structure of $[CoCl_2(Hmhp)_2(H_2O)_2].2Hmhp$, (I), containing a simple mononuclear complex of Hmhp co-crystallized with free Hmhp. Interest in the structure of this material stems from the relationship between the complex and the uncomplexed Hmhp, and from the presence of both complexed and uncomplexed Hmhp within the same structure.



(I)

The octahedral Co centre in (I) occupies a crystallographic inversion centre, and adopts quite typical bond lengths and angles to the Cl, H_2O and Hmhp ligands. The Hmhp binds through the exocyclic O atom and this is also quite normal. Corresponding structural parameters of the complexed and uncomplexed Hmhp molecules are identical to within 2σ for all bonds and angles. The precision of these parameters, which is better than normally obtained in related complexes, is a consequence of the location of the Co atom on a $\bar{1}$ special position in $P2_1/n$ so that it only contributes to the reflection data with $h + k + l = 2n$.

Of somewhat more interest is the formation of a one-dimensional hydrogen-bonded polymer in which the Co complexes alternate with pairs of unbound Hmhp molecules (Fig. 1). The most powerful hydrogen-bond donor and acceptor in this system are O3 (*i.e.* the bound water molecule) and O2 (in the unbound Hmhp), respectively. Consistent with Etter's treatment (1990), these form $R_2^2(8)$ systems disposed about crystallographic inversion centres; these, together with the H_2O—Co bonds, can be considered to form the main backbone of the polymer. Secondary hydrogen bonds then form between the Cl ligands and the protic H atoms of both the bound and unbound Hmhp (Table 2).

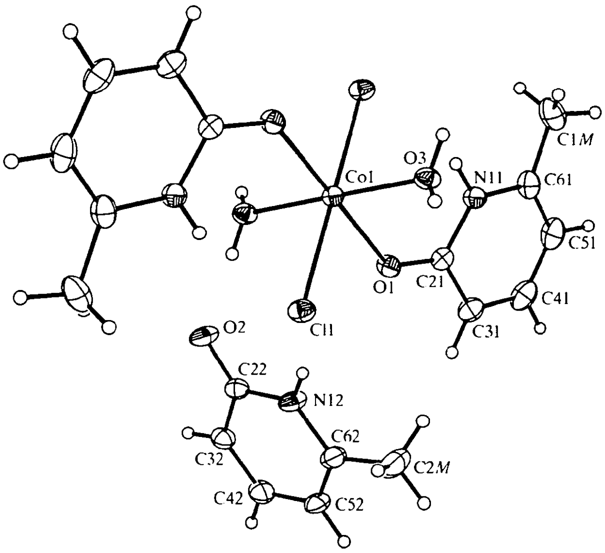


Fig. 1. A view of (I) with the atom-numbering scheme. Displacement ellipsoids enclose 30% probability surfaces.

The variety of complexes formed by pyridonates runs parallel to the variety of binding modes that this ligand can adopt both in its protonated and deprotonated forms. Although it has so far been difficult to discern predictable trends, hydrogen bonding between complexed ligands appears to play a crucial role in stabilizing the large polynuclear arrays which characterize this field. Whenever a pyridonate binds terminally through its exocyclic O atom, the N atom (whether it is protonated or not) is usually involved in hydrogen bonding. In (I), the availability of Hmhp in excess of that required for complex formation, and the presence of more powerful hydrogen-bonding centres than the N atom of the Hmhp, tend to favour the formation of a small mononuclear complex. Greater relative importance of the N atom of a bound mhp or Hmhp as a hydrogen-bond donor or acceptor can be achieved by controlling the stoichiometry of the reaction mixture, by using non-aqueous solvents, by driving off water at high temperature, *etc.* It is under these conditions that the formation of large complexes appears to be most favoured.

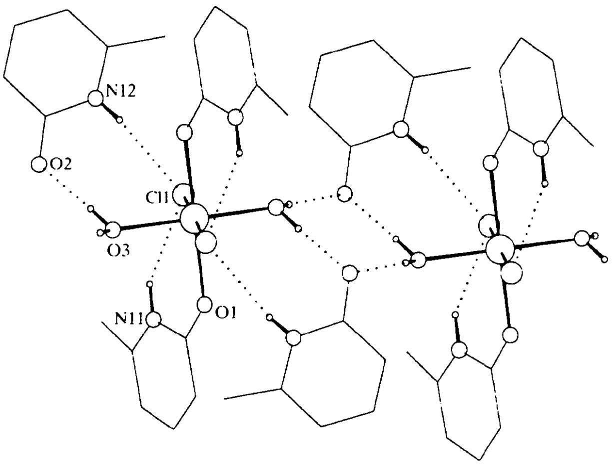


Fig. 2. Formation of a hydrogen-bonded one-dimensional polymer in the crystal structure of (I).

Experimental

Complex (I) was prepared as a by-product of the reaction of $CoCl_2.6H_2O$, Namhp and sodium rhodizonate in methanol. After removal of the solvent, the product was recrystallized from ethyl acetate.

Crystal data

$[CoCl_2(C_6H_7NO)_2(H_2O)_2]$.-
$2C_6H_7NO$
$M_r = 602.37$
Monoclinic
$P2_1/n$
$a = 7.7418\,(6)$ Å
$b = 20.242\,(3)$ Å
$c = 9.4443\,(7)$ Å
$\beta = 109.561\,(6)°$
$V = 1394.6\,(3)$ Å^3
$Z = 2$
$D_x = 1.434$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 56 reflections
$\theta = 15–16°$
$\mu = 0.851$ mm^{-1}
$T = 220\,(2)$ K
Lath
0.39 × 0.21 × 0.08 mm
Pink

Data collection

Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device (Cosier & Glazer, 1986)

2449 independent reflections
1667 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\rm max} = 25.01°$

ω–θ scans with ω half-width $(1.05 + 0.35\tan\theta)^\circ$
Absorption correction:
ψ scans (North *et al.*, 1968)
$T_{\min} = 0.846$, $T_{\max} = 0.934$
2515 measured reflections

$h = -9 \rightarrow 8$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.079$
$S = 1.026$
2446 reflections
187 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.027P)^2 + 0.291P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected bond lengths (Å)*

Co1—O3	2.050 (2)	C31—C41	1.361 (5)
Co1—O1	2.112 (2)	C41—C51	1.402 (5)
Co1—Cl1	2.5011 (8)	C51—C61	1.343 (5)
N11—C21	1.365 (4)	C61—C1*M*	1.490 (5)
N11—C61	1.369 (4)	N12—C22	1.366 (4)
C21—O1	1.265 (4)	N12—C62	1.368 (4)
C21—C31	1.419 (4)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*A*···O2^{i}	0.77 (4)	2.02 (4)	2.758 (4)	161 (4)
O3—H3*B*···O2^{ii}	0.86 (4)	1.86 (4)	2.712 (4)	176 (4)
N11—H11···Cl1^{ii}	0.86 (4)	2.31 (4)	3.104 (3)	152 (4)
N12—H12···Cl1	0.79 (4)	2.49 (4)	3.229 (4)	157 (3)

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x, -y, -z$.

The H atoms attached to sp^2-hybridized C atoms were allowed to ride on their parent atoms with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$; methyl groups were treated as rotating rigid groups with $U_{\rm iso}(\rm H) = 1.5U_{\rm eq}(\rm C)$. The four H atoms attached to N11, N12 and O3 were refined freely.

Data collection: *DIF*4 (Stoe & Cie, 1990*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1990*b*). Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL* and *CAMERON* (Pearce *et al.*, 1994). Software used to prepare material for publication: *PLATON* (Spek, 1997).

We thank the EPSRC for provision of a four-circle diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1364). Services for accessing these data are described at the back of the journal.

References

Blake, A. J., Brechin, E. K., Gilby, L., Gould, R. O., Harris, S. G., Parsons, S. & Winpenny, R. E. P. (1998). *J. Chem. Soc. Dalton Trans.* Submitted.

Brechin, E. K., Harris, S. G., Harrison, A., Parsons, S., Whittaker, A. G. & Winpenny, R. E. P. (1997). *Chem. Commun.* pp. 653–654.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–108.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Parsons, S. & Winpenny, R. E. P. (1997). *Acc. Chem. Res.* **30**, 89–95.

Pearce, L. J., Prout, C. K. & Watkin, D. J. (1994). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

Sheldrick, G. M. (1995). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spek, A. L. (1997). *PLATON. Molecular Geometry Program.* University of Utrecht, The Netherlands.

Stoe & Cie (1990*a*). *DIF*4. *Diffractometer Control Program.* Version 7.09/DOS. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1990*b*). *REDU*4. *Data Reduction Program.* Version 7.03/DOS. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1998). C**54**, 764–766

Trimethylammonium Nickel(II) Chloride Dihydrate

GERHARD THIELE AND GUNNAR WITTENBURG

Materialforschungsinstitut und Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstraße 21, D-79104 Freiburg, Germany. E-mail: witt@sapphire.chemie.uni-freiburg.de

(*Received 9 June 1997; accepted 6 January 1998*)

Abstract

catena-Poly[trimethylammonium [diaquanickel(II)-di-μ-chloro] chloride], $[(CH_3)_3NH][NiCl_2(H_2O)_2]Cl$, is built up by infinite chains of Cl-edge-sharing *trans*-$[NiCl_4(H_2O)_2]$ octahedra separated by trimethylammonium cations and discrete Cl^- anions. The compound is isostructural with the cobalt and manganese compounds, with negligible modifications caused by the difference in the ionic radii of the metal ions. The crystal structure is stabilized by hydrogen bonds between the discrete Cl^- ions and the water molecules, and also between the trimethylammonium ions and the water molecules.

Comment

The title compound is isostructural with the analogous manganese (Caputo *et al.*, 1976) and cobalt (Losee *et al.*, 1973) compounds; they consist of infinite chains of edge-sharing *trans*-$[MCl_4(H_2O)_2]$ octahedra (M = Mn, Co or Ni) running parallel to the *b* axis. These one-dimensional chains make the compounds useful for studying and testing the concepts of prediction of magnetic properties, established by the Ising or Heisenberg theory (De Jongh & Miedema, 1974). The magnetic susceptibilities of powder samples of the one-dimensional $S = 1$ system $[(CH_3)_3NH][NiCl_3].2H_2O$ (O'Brien *et al.*, 1981) have been measured and the data