Table 2. *Selected geometric parameters (Å, °)*

Na—O5′^{i}	2.3077 (15)	N1—C6	1.369 (2)
Na—O92^{ii}	2.382 (2)	N3—C2	1.337 (2)
Na—O2′	2.3849 (13)	N3—C4	1.346 (2)
Na—O93	2.4384 (15)	N7—C8	1.305 (2)
Na—O91	2.4599 (14)	N7—C5	1.398 (2)
Na—O92	2.485 (2)	N9—C8	1.369 (2)
Na···Na^{ii}	3.188 (2)	N9—C4	1.376 (2)
O2′—C2′	1.407 (2)	N9—C1′	1.448 (2)
O3′—C3′	1.426 (2)	C1′—C2′	1.527 (2)
O4′—C1′	1.424 (2)	C2′—C3′	1.527 (2)
O4′—C4′	1.466 (2)	C3′—C4′	1.518 (2)
O5′—C5′	1.420 (2)	C4′—C5′	1.509 (2)
O6—C6	1.273 (2)	C6—C5	1.414 (2)
N1—C2	1.332 (2)	C5—C4	1.386 (2)
C2—N1—C6	119.44 (14)	C8—N9—C4	105.98 (12)
C2—N3—C4	110.46 (12)	N1—C6—C5	115.22 (13)
C8—N7—C5	104.55 (13)	N1—C2—N3	129.85 (14)

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

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2′—H82′···O6^{i}	0.97 (3)	1.77 (3)	2.727 (2)	171 (3)
O3′—H83′···O2′	0.82 (3)	2.30 (4)	2.763 (2)	117 (3)
O3′—H83′···O93	0.82 (3)	2.13 (3)	2.896 (2)	156 (3)
O5′—H85′···N3	0.83 (3)	1.99 (3)	2.802 (2)	166 (4)
O91—H911···O6^{ii}	0.89 (3)	1.93 (3)	2.792 (2)	165 (3)
O92—H921···N1^{iii}	0.96 (3)	2.05 (4)	3.001 (2)	170 (5)
O92—H922···O6	0.70 (3)	2.58 (3)	3.180 (2)	146 (3)
O93—H931···O4′^{iv}	0.88 (3)	1.95 (3)	2.829 (2)	172 (3)
O93—H932···N7	0.83 (3)	2.07 (3)	2.880 (2)	164 (3)
C5′—H52′···O3′^{v}	0.98 (3)	2.41 (3)	3.293 (2)	150 (2)

Symmetry codes: (i) $x, y-1, z$; (ii) $1-x, 2-y, 1+z$; (iii) $x, y-1, 1+z$; (iv) $\frac{3}{2}-x, y-\frac{1}{2}, 1-z$; (v) $\frac{3}{2}-x, \frac{1}{2}+y, -z$.

H atoms were located from a difference map and their positions and $U_{\rm iso}$ values refined.

Data collection: *IPDS Diffractometer Software* (Stoe & Cie, 1993). Cell refinement: *IPDS Diffractometer Software*. Data reduction: *IPDS Diffractometer Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1990).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: SK1041). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bariyanga, J. & Theophanides, T. (1985). *Inorg. Chim. Acta*, **108**, 133–140.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kim, S. H. & Martin, R. B. (1984). *Inorg. Chim. Acta*, **91**, 19–24.
Klüfers, P., Mayer, P. & Schuhmacher, J. (1995). *Z. Anorg. Allg. Chem.* **621**, 1373–1379.
Klüfers, P., Piotrowski, H. & Schuhmacher, J. (1996). *Z. Anorg. Allg. Chem.* In the press.
Lönnberg, H. (1990). *Biocoordination Chemistry*, edited by K. Burger, pp. 284–346. New York: Ellis Horwood.
Munns, A. R. I. & Tollin, P. (1970). *Acta Cryst.* B**26**, 1101–1113.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Sigel, H., Massoud, S. S. & Corfù, N. A. (1994). *J. Am. Chem. Soc.* **116**, 2958–2971.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Stoe & Cie (1993). *Scanner Stoe IPDS Diffractometer Software*. Version 1.08. Stoe & Cie, Darmstadt, Germany.
Subramanian, E. (1979). *Cryst. Struct. Commun.* **8**, 777–785.
Thewalt, U., Bugg, C. E. & Marsh, R. E. (1970). *Acta Cryst.* B**26**, 1089–1101.

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A Homoleptic Cuprate(II) Complex with Deprotonated 1,6-Anhydro-β-D-glucose (Levoglucosan) Ligands†

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Abstract

The cuprate anion in the title complex, dilithium bis[1,6-anhydro-β-D-glucosidato(2−)-O^2,O^4]cuprate(II) octahydrate, $Li_2[Cu(C_6H_8O_5)_2].8H_2O$, is a homoleptic mononuclear 1,3-polyolato(2−) complex. The ligator atoms of the levoglucosan ligand are closer together by *ca* 0.4 Å with respect to the uncomplexed 1,3-diol moiety of the anhydro sugar, thus exhibiting an enhanced flexibility compared with 1,2-diols.

Comment

The 'bite' of a chelate ligand is of limited variability, particularly when the ligator atoms are attached to a further cyclic fragment, above all, to a six-membered ring in its energetically favoured chair conformation. In the coordination chemistry of carbohydrates, this general statement may be quantified for 1,2-

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† Polyol Metal Complexes. 20. For part 19, see Klüfers & Mayer (1996).

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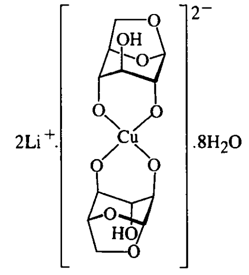
diol fragments incorporated in pyranose rings. In Cu^{II} or Co^{III} complexes of the methyl glycopyranosides of β-D-galactose (Burger & Klüfers, 1995), α-D-mannose (Habermann, Jung, Klaassen & Klüfers, 1992; Habermann, Klaassen & Klüfers, 1993; Burger & Klüfers, 1995) and β-D-xylose (Klaassen & Klüfers, 1994), the mean $O\cdots O$ distance of the ligating diol groups is 2.665 ± 0.014 Å. This corresponds to a 0.186 Å reduction of the respective mean distance of 2.851 ± 0.023 Å in the uncomplexed methyl glycopyranosides [β-D-galactose (Sheldrick, 1977; Takagi & Jeffrey, 1978), α-D-mannose (Gatehouse & Poppleton, 1970) and β-D-xylose (Takagi & Jeffrey, 1977)].

With the assumption that a bicyclic pyranoid carbohydrate will also be of restricted flexibility, the ease of complexation of cupric ions by 1,6-anhydro-β-D-glucose [levoglucosan; symbol according to IUPAC–IUB Joint Commission on Biological Nomenclature Recommendations 1980 (1982): 1,6AnGlc] in alkaline aqueous solution was unexpected due to the unfavourably large $O\cdots O$ separation of 3.299 Å in the free ligand (Park, Kim & Jeffrey, 1971). The structure of the title compound, $Li_2[Cu(1,6AnGlc2,4H_{-2})_2].8H_2O$, (I), was examined in order to clarify the bonding mode of the ligand.



(I)

In the mononuclear cuprate(II) ions in the title compound, 4+2 coordinated cupric ions form six-membered chelate rings with doubly deprotonated levoglucosan ligands at a shorter Cu—O distance. Two longer contacts are established with the O5 atoms of the pyranose rings. The anhydro sugar thus resembles the well known 1,2-diolate(2−) anions mentioned above in the sense of forming simple chelate rings with its 1,3-diolate moiety. The chelate bonding mode is enabled by an obviously enhanced flexibility of the bicyclic ligand compared with simple pyranoses. This is demonstrated by a twofold reduction of the ligator atom distance on coordination (0.377 Å) compared with the above-mentioned 1,2-diolates. A reason for levoglucosan being a ligand with a more variable 'bite' is that in the strained bicyclic anhydro sugar, the conformational path ${}^1C_4 = {}^3C_{O5} \rightarrow {}^3B_{O5}$ appears to be flat with respect to conformational energy. In the first steps of the conformational transition, atom O3 is tilted towards the equatorial plane and atoms O2 and O4 move apart. In crystalline levoglucosan itself, this transition has taken place to an extent, which may be characterized alternatively by the $O2\cdots O4$ distance of 3.3 Å or by the puckering phase angle θ (Cremer & Pople, 1975) of the pyranose ring of 154.6° in the uncomplexed carbohydrate (*cf.* 180° for the ideal ${}^1C_4$ chair conformation of a D-pyranose ring and 90° for a boat conformation). Thus, in the title

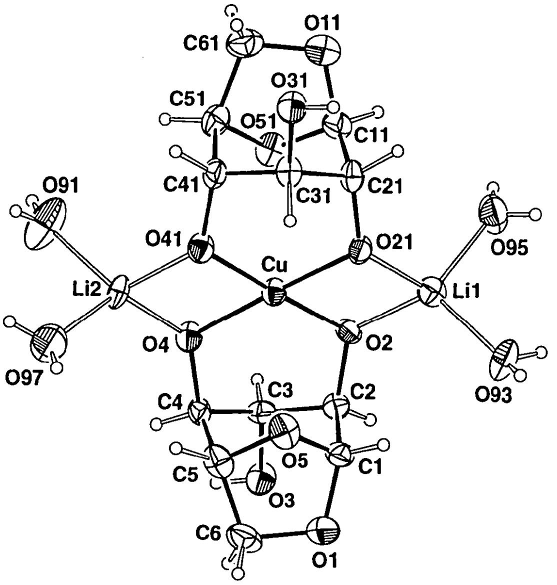


Fig. 1. The structure of the $Li_2(H_2O)_4Cu(Glc1,6An2,4H_{-2})_2$ moiety (50% probability displacement ellipsoids).

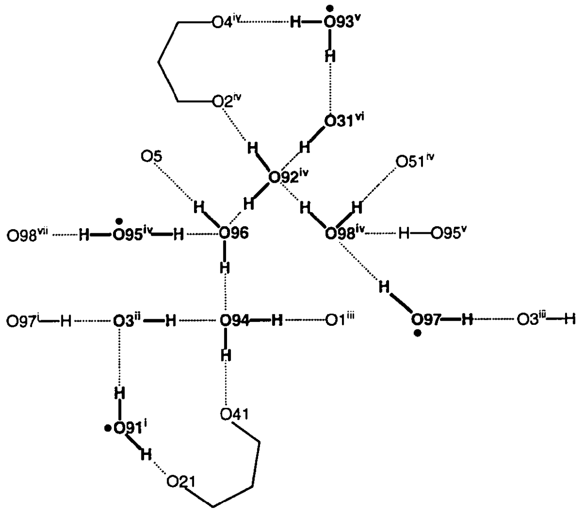


Fig. 2. The hydrogen-bonding structure in (I). Water O atoms are coded O9*n* (*n* = 1–8). Bold text indicates donor groups with all next neighbours; water molecules coordinating to lithium are denoted by a dot; arrows indicate the infinite cooperative chain along [100]. Symmetry codes are according to *x*, *y*, *z* + (i) 100; (ii) 010; (iii) $\bar{1}10$; (iv) 001; (v) $\bar{1}01$; (vi) $0\bar{1}\bar{1}$; (vii) 101.

compound, a closer approach to the ideal chair conformation has taken place in the course of the complexation (mean value of θ is 160.6°). A peculiarity of complex (I) is highlighted in Fig. 1, *i.e.* each cuprate dianion is associated with two diaqua–lithium counterions *via* edge sharing of the respective coordination polyhedra, thus forming an electrically neutral aggregate. The three-dimensional structure is determined by a hydrogen-bond structure (Jeffrey & Saenger, 1991) which is built up from neutral aggregates and four additional water molecules per lithium cuprate moiety. The hydrogen-bond structure is characterized by finite cooperative sequences (Fig. 2), the main constituents of which are those water molecules not bonded to Li ions.

Experimental

Cupric hydroxide (0.3 g, 3.08 mmol), 1,6-anhydro-β-D-glucopyranose (levoglucosan; 1 g, 6.16 mmol), water (0.6 g) and lithium hydroxide solution (2.46 ml; 5 mol l^{-1} = 12.32 mmol) were combined to give a dark-green solution. After addition of ethanol (3.46 ml), blue crystals were formed over a period of one week at *ca* 278 K. Contact with oxygen and light was prevented [f.p.(dec.) = 371 K].

Crystal data

$Li_2[Cu(C_6H_8O_5)_2].8H_2O$
$M_r = 541.80$
Triclinic
$P1$
$a = 7.732\ (4)$ Å
$b = 8.879\ (6)$ Å
$c = 9.772\ (8)$ Å
$\alpha = 66.92\ (6)°$
$\beta = 85.13\ (6)°$
$\gamma = 64.39\ (4)°$
$V = 553.6\ (7)$ Å^3
$Z = 1$
$D_x = 1.625$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 283 reflections
$\theta = 7–18°$
$\mu = 1.071$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.22 × 0.15 × 0.11 mm
Blue

Data collection

Stoe IPDS diffractometer
φ scans, area detector
Absorption correction: none
4250 measured reflections
3522 independent reflections

3416 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0354$
$\theta_{max} = 26°$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R(F) = 0.0342$
$wR(F^2) = 0.0899$
$S = 1.067$
3521 reflections
410 parameters
All H-atom parameters refined

$\Delta\rho_{max} = 0.240$ e Å^{-3}
$\Delta\rho_{min} = -0.397$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

$w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 0.5354P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

Absolute configuration: Flack (1983)
Flack parameter = −0.012 (14)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu	0.49965 (8)	0.49990 (8)	0.50022 (6)	0.02267 (12)
O1	0.9010 (6)	−0.0235 (6)	0.8485 (4)	0.0389 (10)
O2	0.7035 (5)	0.2936 (5)	0.4622 (4)	0.0239 (9)
O3	0.6636 (6)	−0.1160 (6)	0.7118 (5)	0.0314 (9)
O4	0.3510 (5)	0.3684 (5)	0.6135 (4)	0.0264 (9)
O5	0.7026 (6)	0.2765 (6)	0.7532 (4)	0.0323 (9)
O11	0.3166 (6)	0.9833 (6)	0.0678 (4)	0.0423 (10)
O21	0.6541 (5)	0.6271 (5)	0.3944 (4)	0.0245 (8)
O31	0.3505 (6)	1.1114 (5)	0.2927 (4)	0.0317 (9)
O41	0.2923 (5)	0.7119 (6)	0.5303 (4)	0.0277 (9)
O51	0.3092 (6)	0.7260 (6)	0.2399 (4)	0.0306 (9)
C1	0.8474 (8)	0.1403 (8)	0.7143 (6)	0.0283 (12)
C2	0.7633 (8)	0.1234 (8)	0.5858 (5)	0.0236 (11)
C3	0.5931 (8)	0.0792 (8)	0.6285 (6)	0.0259 (12)
C4	0.4624 (7)	0.1875 (7)	0.7163 (6)	0.0250 (11)
C5	0.5819 (8)	0.1886 (9)	0.8322 (5)	0.0311 (13)
C6	0.7338 (9)	0.0048 (9)	0.9322 (6)	0.0385 (13)
C11	0.4380 (8)	0.8048 (8)	0.1706 (6)	0.0316 (13)
C21	0.5504 (8)	0.8051 (8)	0.2918 (6)	0.0251 (11)
C31	0.4134 (7)	0.9215 (8)	0.3740 (6)	0.0236 (11)
C41	0.2371 (8)	0.8802 (8)	0.4079 (6)	0.0278 (13)
C51	0.1587 (8)	0.8779 (8)	0.2703 (6)	0.0308 (12)
C61	0.1321 (9)	1.0359 (9)	0.1239 (6)	0.0396 (13)
Li1	0.8561 (14)	0.4245 (14)	0.3644 (10)	0.028 (2)
Li2	0.1470 (13)	0.5750 (14)	0.6342 (11)	0.029 (2)
O91	−0.1116 (7)	0.6703 (8)	0.5484 (6)	0.0598 (15)
O92	0.6192 (9)	0.2445 (9)	0.2253 (6)	0.0544 (13)
O93	1.1149 (5)	0.3229 (6)	0.4498 (5)	0.0407 (10)
O94	0.3745 (7)	0.7688 (8)	0.7623 (5)	0.0485 (12)
O95	0.8929 (5)	0.4867 (6)	0.1539 (4)	0.0452 (9)
O96	0.6991 (7)	0.4570 (7)	0.9426 (4)	0.0515 (11)
O97	0.0703 (6)	0.5986 (6)	0.8233 (4)	0.0539 (12)
O98	0.2397 (7)	0.5388 (6)	0.0927 (5)	0.0508 (10)

Table 2. *Selected geometric parameters (Å, °)*

Cu—O41	1.986 (4)	O21—Li1	1.915 (11)
Cu—O4	1.960 (4)	O41—Li2	1.947 (10)
Cu—O2	1.979 (4)	Li1—O93	1.910 (11)
Cu—O21	1.952 (4)	Li1—O95	1.940 (10)
O2—Li1	1.944 (10)	Li2—O91	1.919 (11)
O4—Li2	1.905 (10)	Li2—O97	1.955 (11)
C11—O51—C51	100.2 (4)	O51—C51—C61	101.0 (5)
O5—C5—C6	100.5 (4)	C61—C51—C41	116.2 (6)
C6—C5—C4	115.6 (5)		

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H831···O94^{i}	0.83 (7)	2.05 (7)	2.772 (8)	145 (8)
O31—H832···O92^{ii}	0.83 (7)	1.93 (7)	2.725 (10)	161 (9)
O91—H911···O3^{iii}	0.82 (6)	2.09 (6)	2.868 (8)	158 (6)
O91—H912···O21^{iv}	0.83 (7)	1.87 (7)	2.685 (8)	171 (7)
O92—H921···O2	0.83 (6)	1.87 (6)	2.696 (8)	178 (8)
O92—H922···O96^{v}	0.83 (5)	2.06 (4)	2.864 (8)	165 (6)
O93—H931···O4^{vi}	0.83 (8)	1.95 (7)	2.774 (7)	170 (8)
O93—H932···O31^{vii}	0.82 (7)	2.05 (7)	2.834 (7)	159 (7)
O94—H941···O41	0.83 (8)	1.87 (7)	2.687 (7)	168 (7)
O94—H942···O1^{iii}	0.83 (6)	2.73 (6)	3.517 (9)	160 (5)
O95—H951···O96^{v}	0.81 (6)	2.01 (6)	2.806 (7)	166 (7)
O95—H952···O98^{vi}	0.82 (6)	2.08 (6)	2.889 (8)	174 (7)
O96—H961···O94	0.83 (5)	2.01 (6)	2.826 (8)	165 (5)
O96—H962···O5	0.83 (7)	2.31 (7)	2.877 (7)	126 (6)
O97—H971···O98^{viii}	0.83 (6)	2.02 (6)	2.796 (7)	155 (6)
O97—H972···O3^{iii}	0.83 (5)	2.23 (6)	3.004 (8)	155 (6)

O98—H981···O51	0.83 (6)	2.03 (6)	2.810 (8)	158 (6)
O98—H982···O31^i	0.82 (5)	2.78 (6)	3.258 (8)	119 (4)
O98—H982···O92	0.82 (5)	2.11 (5)	2.912 (10)	166 (6)

Symmetry codes: (i) $x, y-1, z$; (ii) $x, 1+y, z$; (iii) $x-1, 1+y, z$; (iv) $x-1, y, z$; (v) $x, y, z-1$; (vi) $1+x, y, z$; (vii) $1+x, y-1, z$; (viii) $x, y, 1+z$.

H atoms were located from a difference map and their positions were refined. Restraints on oxygen-bound H atoms involved one common U, a unique O—H distance for all H atoms and H—H distances in the water molecules restrained to the 1.58-fold of the O—H distance (corresponding to a 105° angle). The common O—H distance refined to 0.828 (14) Å.

Data collection: *IPDS Diffractometer Software* (Stoe & Cie, 1993). Cell refinement: *IPDS Diffractometer Software*. Data reduction: *IPDS Diffractometer Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1982). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1042). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Burger, J. & Klüfers, P. (1995). *Chem. Ber.* **128**, 75–79.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Gatehouse, B. M. & Poppleton, B. J. (1970). *Acta Cryst.* B**26**, 1761–1765.
Habermann, N., Jung, G., Klaassen, M. & Klüfers, P. (1992). *Chem. Ber.* **125**, 809–814.
Habermann, N., Klaassen, M. & Klüfers, P. (1993). *Carbohydr. Res.* **241**, 9–23.
IUPAC-IUB Joint Commission on Biological Nomenclature Recommendations 1980 (1982). *Eur. J. Biochem.* **126**, 433–437.
Jeffrey, G. A. & Saenger, W. (1991). In *Hydrogen Bonding in Biological Structures*. Berlin, Heidelberg, New York: Springer-Verlag.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Klaassen, M. & Klüfers, P. (1994). *Z. Anorg. Allg. Chem.* **620**, 1631–1634.
Klüfers, P. & Mayer, P. (1996). *Acta Cryst.* C**52**, 2970–2972.
Park, Y. J., Kim, H. S. & Jeffrey, G. A. (1971). *Acta Cryst.* B**27**, 220–227.
Sheldrick, B. (1977). *Acta Cryst.* B**33**, 3003–3005.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1982). *The EUCLID Package. Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.
Stoe & Cie (1993). *Scanner Stoe IPDS Diffractometer Software*. Version 1.08. Stoe & Cie, Darmstadt, Germany.
Takagi, S. & Jeffrey, G. A. (1977). *Acta Cryst.* B**33**, 3033–3040.
Takagi, S. & Jeffrey, G. A. (1978). *Acta Cryst.* B**34**, 2006–2010.

Acta Cryst. (1996). C**52**, 2975–2977

Tetrachloro[2-(phenylamino)pyridinato]titanate(IV) with a 2-(Phenylamino)pyridinium Counterion

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Abstract

The title salt, 2-(phenylamino)pyridinium tetrachloro[2-(phenylamino)pyridinato-N,N']titanate(IV), $(C_{11}H_{11}N_2)$-$[TiCl_4(C_{11}H_9N_2)]$, is a product of the reaction of titanium tetrachloride and 2-(phenylamino)pyridine. The coordinated deprotonated aminopyridine forms a four-membered chelate ring. Titanium has a pseudo-octahedral coordination sphere. A second 2-(phenylamino)pyridine residue behaves as a proton acceptor and is a counterion in the solid state.

Comment

Amido complexes of early transition metals are commonly synthesized *via* transmetallation reactions. Over 60 years ago, tetrakis(diphenylamido)titanium was obtained as a product of the reaction of potassium diphenylamide and $TiCl_4$ (Dermer & Fernelius, 1934). Lithium reagents have most commonly been used in the syntheses of both homoleptic (Bradley & Thomas, 1960) and heteroleptic amido complexes, such as mixed-halide complexes of the type $(R_2N)_y\mathrm{Ti}X_{4-y}$ (y = 1–3; R = Me, Et; X = Cl, Br, I) (for review see Bürger & Neese, 1970). Various amido complexes have also been prepared by refluxing $TiCl_4$ with primary or secondary amines (Cowdell & Fowles, 1960).

It has been shown recently that both the chloro(dimethylamido)bis(aminopyridinato)titanium and chlorotris(aminopyridinato)titanium complexes can be prepared with high yields using $[TiCl_2(Me_2N)_2(thf)_2]$ (thf is tetrahydrofuran) as a starting material (Kempe & Arndt, 1996). This method is particularly useful because lithium aminopyridinates were reported to form the desired transition metal complexes with only very low yields. A limitation of the amine-exchange reaction is that only monochloro complexes, such as chlorotris[2-(phenylamino)pyridinato]titanium and chloro(dimethylamido)bis[2-(phenylamino)pyridinato]titanium, can be obtained.

In our attempt to find synthetic routes to dichloroaminopyridinate complexes, four equivalents of 2-

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