The *E* statistics were generally indicative of a centrosymmetric space group, but the systematic absences were only consistent with the non-centrosymmetric space groups $I\bar{4}2d$ and $I4_1md$. From the Patterson function, it seemed highly probable that most or all of the heavy atoms resided on special positions, and a consideration of the possible geometry of the complex led to the likelihood of the former space group. However, all initial attempts to solve the structure led to unsatisfactory refinements, with some of the light-atom positions being undetectable in difference Fourier maps. The structure was finally solved using the *DIRDIF*96 package (Beurskens *et al.*, 1996). The rather diffuse, but quite substantial, electron density from the disordered pentaiodide anion and the presence of the heavy atoms on special positions were undoubtedly the major reasons for the original failure to solve the structure completely. Indeed, only when the disordered pentaiodide was satisfactorily modelled was it possible to detect all of the light-atom positions of the hmpa ligand from difference Fourier maps. The final refinement of the structure proceeded smoothly, with the largest correlation matrix element (0.66) relating the displacement-parameter elements of atom I21. Calculations using *PLATON* (Spek, 1990) indicated that there were no further voids in the structure capable of containing solvent molecules.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1992). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *XCAD*-4 (Harms & Wocadlo, 1996). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*3 for Windows (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1163). Services for accessing these data are described at the back of the journal.

References

Bailey, R. D. & Pennington, W. T. (1995). *Acta Cryst.* B**51**, 810–815.
Beurskens, P. T., Beurskens, G., Bosman, W. P., de Gelder, R., García-Granda, S., Gould, R. O., Israel, R. & Smits, J. M. M. (1996). *The DIRDIF96 Program System*. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.
Blake, A. J., Gould, R. O., Parsons, S., Radek, C. & Schröder, M. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2374–2376.
Clegg, W., Farrugia, L. J., McCamley, A., Norman, N. C., Orpen, A. G., Pickett, N. L. & Stratford, S. E. (1993). *J. Chem. Soc. Dalton Trans.* pp. 2579–2587.
Dong, T.-Y., Lin, H.-M., Hwang, M.-Y., Lee, T.-Y., Tseng, L.-H., Peng, S.-M. & Lee, G.-H. (1991). *J. Organomet. Chem.* **414**, 227–244.
Enraf–Nonius (1992). *CAD*-4 *EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Harms, K. & Wocadlo, S. (1996). *XCAD-4. Program for Processing CAD-4 Diffractometer Data*. University of Marburg, Germany.
Hills, A., Hughes, D. L., Leigh, G. J. & Sanders, J. R. (1991). *J. Chem. Soc. Dalton Trans.* pp. 61–64.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Tebbe, K.-F. & Gilles, T. (1996). *Z. Anorg. Allg. Chem.* **622**, 138–143.
Watkin, D. M., Pearce, L. & Prout, C. K. (1993). *CAMERON*. Chemical Crystallography Laboratory, University of Oxford, England.

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fac-Triazido(2,2′-bipyridine-*N*,*N*′)(pyridine-*N*)cobalt(III)

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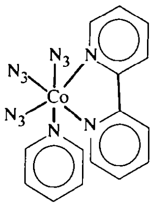
Abstract

The title complex, $[Co(N_3)_3(C_{10}H_8N_2)(C_5H_5N)]$, adopts *fac*-octahedral coordination geometry. All the azido ligands are terminally coordinated with an average Co—N—N angle of 125°. The pyridine ligand is least strongly coordinated to the Co^{III} atom and forms the longest Co—N bond [1.992 (2) Å]. The bipyridine rings lie in the equatorial plane and are nearly perpendicular to the pyridine ring.

Comment

The number of known first-row transition metal complexes containing azido ligands has markedly increased in the past few years; their number now includes low-dimensional complexes of copper (Thompson *et al.*, 1995, and references therein), nickel (Escuer *et al.*, 1995, and references therein) and manganese (Cortes *et al.*, 1997). The main interest arises from the rich magnetic chemistry of these azido complexes, which depends on whether the coordination mode of the ligand is end-on (Charlot *et al.*, 1986) or end-to-end (Escuer, Vincente, El Fallah *et al.*, 1996). We have become interested in this type of complex recently (Chen, Qiu *et al.*, 1994; Chen, Tang *et al.*, 1994) and now report the crystal structure of a discrete mononuclear Co^{III} complex, (I), containing three azido ligands, with pyridine and bipyridine as co-ligands.



(I)

The Co^{III} ion in the title compound (Fig. 1) is octahedrally coordinated by six N atoms: three from the three independent terminally ligated azido groups, two from the bipyridine molecule and one from pyridine. The Co—N(pyridine) bond [1.992 (2) Å] is longer than the Co—N(bipyridine) bonds [1.962 (2) and 1.963 (2) Å], which are in turn longer than the Co—N(azide) bonds [1.915 (2)–1.941 (2) Å]. The five-membered chelate ring formed by the 2,2′-bipyridine ligand with the Co atom is planar and forms a dihedral angle of 87.3° with the pyridine ring. The azido groups are all terminally coordinated to the Co atom, with an average Co—N*n*1 (*n* = 1, 2, 3) distance of 1.929 Å, which is rather short compared with those in $[Co(N_3)(PMe_3)_3Me_2]$ [2.071 (4) Å] and $[Co(N_3)(PMe_3)_2(CO)_2]$ [2.029 (5) Å] (Chiu *et al.*, 1984), and even shorter than those in the similarly coordinated complexes $[Co(py)_3(N_3)_3]$ and $[Co(3\text{-Mepy})_3(N_3)_3]$ (1.950 Å) (Goher *et al.*, 1992). The average Co—N*n*1—N*n*2 angle of 125° is also quite small compared either with values for bridging azides {*e.g.* in $[Mn(\text{ethyl isonicotinate})_2(N_3)_2]_n$, Mn—N—N is 139.7° (Escuer, Vincente, Goher *et al.*, 1996), and in $[Ni(1,3\text{-diamino-2,2-dimethylpropane})_2(N_3)]_n(PF_6)_n$, Ni—N—N is 136.5° (Monfort *et al.*, 1996)} or with values found in other complexes with terminal azide ligands {*e.g.* $[Co(N_3)(PMe_3)_2(CO)_2]$}. However, a comparable value is found for the corresponding angle in $[Co(N_3)(PMe_3)_3Me_2]$ (125.6°). The N*n*1—N*n*2—N*n*3 angles, with an average value of 175.3°, deviate from linearity by nearly 5°, as is usually observed for mononuclear Co^{III}–azide complexes, while in $[Ni(1,3\text{-diamino-2,2-dimethylpropane})_2(N_3)]_n(PF_6)_n$, the azide groups are linear (Monfort *et al.*, 1996).

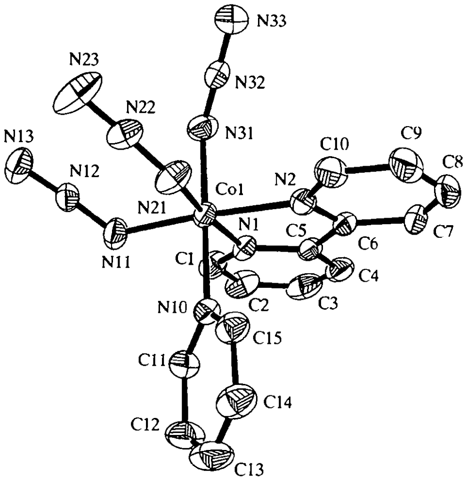


Fig. 1. The molecular structure of the title compound with displacement ellipsoids at the 30% probability level. H atoms have been omitted.

Experimental

Crystals of the title complex were obtained from the reaction of anhydrous $CoCl_2$ with NaN_3 in the presence of 2,2′-bipyridine and pyridine in a molar ratio of 1:2:1:1 in methanol solution at room temperature.

Crystal data

$[Co(N_3)_3(C_{10}H_8N_2)(C_5H_5N)]$
$M_r = 420.30$
Monoclinic
$C2/c$
$a = 25.049\ (4)$ Å
$b = 9.043\ (1)$ Å
$c = 15.956\ (2)$ Å
$\beta = 102.20\ (1)°$
$V = 3532.7\ (8)$ Å^3
$Z = 8$
$D_x = 1.581$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 10–21°$
$\mu = 1.002$ mm^{-1}
$T = 293\ (2)$ K
Octahedral
0.45 × 0.40 × 0.30 mm
Black

Data collection

Siemens diffractometer
$\omega/2\theta$ scans (speed 4–60° min^{-1} in ω)
Absorption correction: none
7201 measured reflections
3620 independent reflections
2639 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$
$\theta_{\max} = 27.49°$
$h = -31 \rightarrow 31$
$k = 0 \rightarrow 9$
$l = -20 \rightarrow 20$
3 standard reflections every 150 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.035$
$wR(F^2) = 0.036$
$S = 1.083$
3620 reflections
254 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 0.5578P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Background measurements were made with stationary crystal and stationary counter at the beginning and end of the scan, each for 25% of the total scan time. Since absorption correction was deemed unnecessary ($\mu r < \frac{1}{2}$), ψ scans were not measured. The H atoms were located in difference maps, though they were later fixed in idealized geometries and allowed to ride.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1361). Services for accessing these data are described at the back of the journal.

References

Charlot, M. F., Kahn, O., Chaillet, M. & Larrieu, C. (1986). *J. Am. Chem. Soc.* **24**, 2574–2581.
Chen, Z.-N., Qiu, J., Wu, Z.-K., Fu, D.-G., Yu, K.-B. & Tang, W.-X. (1994). *J. Chem. Soc. Dalton Trans.* pp. 1923–1927.
Chen, Z.-N., Tang, W.-X. & Yu, K.-B. (1994). *Polyhedron*, **13**, 783–789.
Chiu, K.-W., Wilkinson, G., Thornton-Pett, M. & Hursthouse, M. B. (1984). *Polyhedron*, **3**, 79–84.
Cortes, R., Drillon, M., Solans, X., Lezama, L. & Rolo, T. (1997). *Inorg. Chem.* **36**, 677–683.
Escuer, A., Vicente, R., El Fallah, M. S., Solans, X. & Font-Bardia, M. (1996). *J. Chem. Soc. Dalton Trans.* pp. 1013–1019.
Escuer, A., Vicente, R., Goher, M. A. S. & Mautner, F. A. (1996). *Inorg. Chem.* **35**, 6386–6391.
Escuer, A., Vicente, R., Ribas, J. & Solans, X. (1995). *Inorg. Chem.* **34**, 1793–1798.
Goher, M. A. S., Wang, R.-J. & Mak, T. C.-W. (1992). *Polyhedron*, **11**, 829–837.
Monfort, M., Ribas, J., Solans, X. & Fonf-Bardia, M. (1996). *Inorg. Chem.* **35**, 7633–7638.
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.
Thompson, L. K., Tandon, S. S. & Manuel, M. E. (1995). *Inorg. Chem.* **34**, 2356–2366.

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Dipyridiniomethane *cis*-Dibromotetrafluoroosmate(IV), *cis*-$[(C_5H_5N)_2CH_2][OsBr_2F_4]$

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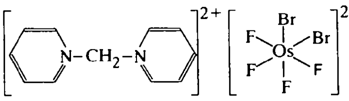
Abstract

The title compound is an *AB*-type salt with a completely ordered anion sublattice. Because of the strong *trans* influence of the Br ligands, both Os—Br bonds, of 2.466 (1) and 2.468 (1) Å, are shortened compared with those reported for $K_2[OsBr_6]$ (2.51 Å). However, only one of the two F ligands coordinated *trans* to a Br ligand exhibits a longer Os—F distance [1.968 (4) Å] than those along the symmetrically coordinated F—Os—F axis [1.930 (4) and 1.929 (4) Å].

Comment

Until recently, species of mixed octahedral hexahalogeno complexes of transition metals have been characterized mainly by their spectroscopic properties (IR, Raman, UV–visible, NMR). Data from X-ray structure determinations have not been available in most cases because of partial or total disorder of the complex anions (Keller & Homborg, 1976). In the past few years, this problem was overcome by studying salts with the dipyridiniomethane dication $[(C_5H_5N)_2CH_2]^{2+}$. *AB*-type salts of this doubly-charged cation with a doubly-charged heteroleptic anion usually have ordered sublattices of both the dications and dianions. This has been attributed to the high steric flexibility of the dication. Thus, it has been possible to determine the structures of nearly all species of the well known mixed chlorofluoroosmates(IV) (Preetz *et al.*, 1984) and chlorofluoroplatinates(IV) (Preetz & Erlhöfer, 1989; Parzich *et al.*, 1993) by single-crystal X-ray structure diffraction (Bruhn, 1995; Bruhn & Preetz, 1994*a*,*b*, 1995, 1996; Bruhn *et al.*, 1995).



(I)

This is the first report of a completely ordered structure of a mixed bromofluoroosmate(IV) which has already been characterized by NMR and vibrational spectroscopy (Höhling, 1996). The complex anion was separated by ion-exchange chromatography from a mixture of bromofluoroosmates(IV), which was obtained by a stereospecific oxidative ligand-exchange reaction of hexabromoosmate(IV) with BrF_3 or $KBrF_4$. The structure of (I) is isotypic with the structure of dipyridiniomethane *cis*-dichlorotetrafluoroosmate(IV) (Bruhn & Preetz, 1994*a*); the dimensions of the monoclinic unit cell are only slightly different. The asymmetric unit with its labelling scheme is presented in Fig. 1.

The octahedral complex anion has approximately C_{2v} local symmetry. Since the *trans* influence of Br ligands is greater than that of F ligands, the Os—Br distances of 2.466 (1) and 2.468 (1) Å are shortened compared with those reported for $K_2[OsBr_6]$ (2.51 Å; McCullough, 1934). However, only one of the two F ligands coordinated *trans* to a Br ligand exhibits a longer Os—F bond [Os—F2 1.968 (4) Å] compared with the lengths of 1.930 (4) and 1.929 (4) Å for the distances along the symmetrically coordinated F3—Os—F4 axis; in contrast, the Os—F1 distance of 1.928 (4) Å is very