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A chloride ion contained in a cobalt 'claw': $[Co_3(DADIT)_3]Cl(PF_6)_2$

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A trimeric compound containing Co^{II} is described, namely tris{μ-2-[3-(dimethylamino)propylimino]propane-1-thiolato}-tricobalt(II) chloride bis(hexafluorophosphate), $[Co_3(C_{10}H_{21}N_2S)_3]Cl(PF_6)_2$. Each Co atom is ligated by one 2-[3-(dimethylamino)propylimino]propane-1-thiolate ligand, an amine group and an imine group. The thiolate groups bridge the Co atoms, forming a six-membered ring that encloses the chloride ion in a well defined binding pocket.

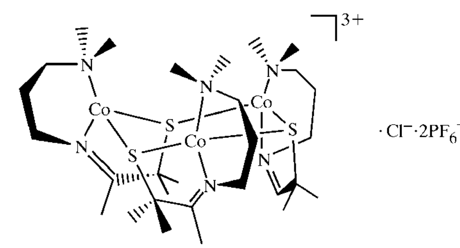
Comment

Host–guest chemistry has received a considerable amount of attention in recent years owing to its importance in biological, material and environmental chemistry (Mueller *et al.*, 1995; Rebek, 2000; Hof *et al.*, 2002). The selective recognition and non-covalent binding of cations is well documented, and numerous systems that perform this function have been prepared. In contrast, comparatively few systems have been prepared that will recognize and non-covalently bind anions (Schmidtchen, 1997). It was reasoned that a metal complex with a well defined electrostatic binding pocket would make an excellent candidate for such an application.

The title compound, $[Co_3(DADIT)_3]Cl(PF_6)_2$, (I), where DADIT is 2-[3-(dimethylamino)propylimino]propane-1-thiolate, was produced from the reaction of $CoCl_2$, *N*,*N*-dimethylpropane-1,3-diamine, 3-mercapto-3-methylbutan-2-one (Shoner *et al.*, 1998) and ferrocenium hexafluorophosphate in acetonitrile. The crystals of (I) were soluble in a number of solvents, including acetonitrile, methanol and dichloromethane.

Compound (I) crystallized in space group $P2_1/n$, with four trimers per unit cell. Each asymmetric unit contains two PF_6^- anions, one well ordered chloride anion and one cobalt trimer (Fig. 1). The complex cation contains three Co^{II} atoms in a distorted tetrahedral coordination environment, each ligated by two N atoms and two thiolate ligands. Each thiolate group bridges two Co atoms.

Three bridging thiolate ligands and three Co atoms form a well defined six-membered ring in which the Co—S bond lengths range from 2.2593 (7) to 2.3237 (7) Å [mean 2.292 (1) Å; Table 1]. This mean bond length falls in the range expected for a Co^{II}–thiolate bond in this ligand environment (Shoner *et al.*, 1998). The average Co—S—Co bond angle is 100.01 (3)°, while the average S—Co—S bond angle is 132.6 (6)°, and thus the mean bond angle for the six-membered ring is 116°, which is comparable to the angle of 109° that would be expected in the idealized geometry of this ring system.



(I)

The Co atoms in the six-membered ring are puckered above the mean plane. Ligated to the Co atoms and directly above this mean plane are the dimethylamine N atoms of the DADIT ligand. The average Co—N(Me_2) bond distance is 2.086 (3) Å, which is consistent with that expected for a Co^{II}—N bond in similar ligand environment (Shoner *et al.*, 1998). These N atoms, along with the cobalt ions, form an electropositively charged pocket that could allow for non-covalent anion binding. The methyl groups of the three NMe_2 groups sit above this electropositive pocket and are oriented parallel to the Co_3S_3 ring, thus forming a hydrophobic ring. This ring could exhibit similar behavior to that found in membrane proteins, by shielding the polar inner pocket from interactions with the solvent, which both increases the solubility of (I) in less polar solvents and further enhances the stability of the pocket–anion interaction (Spudich, 2000).

Contained in this well defined claw-like setting is a chloride anion, which rests intermediate between the cobalt ions and

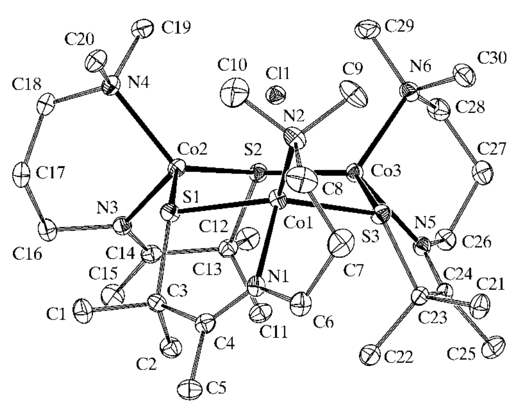


Figure 1
A view of the complex cation and chloride anion of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

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amine N atoms. The average distance between the Co atoms and chloride ion is 2.67 (4) Å, and the average distance between the chloride ion and atoms N2, N4 and N6 is 3.48 (4) Å. Thus, the Cl atom is well out of bonding distance for both the N and the Co atoms, which indicates that the chloride ion is associated in the binding pocket through a Coulomb interaction and not a covalent bond. All studies performed thus far have indicated that the chloride ion will not exchange for other anions, thus indicating that the chloride anion is tightly bound in the binding pocket. Studies aimed at generating other complexes of similar structure with different anions are currently under way.

Experimental

For the preparation of (I), 3-mercapto-3-methylbutan-2-one (472 mg, 4 mmol) in acetonitrile (10 ml) was added to a stirred solution of NaOMe (216 mg, 4 mmol) in acetonitrile (10 ml). The mixture was stirred for 10 min and then anhydrous $CoCl_2$ (258 mg, 2 mmol) in methanol (20 ml) was added dropwise. A brick-red precipitate formed immediately. To this precipitate was added *N*,*N*′-dimethylpropane-1,3-diamine (408 mg) in acetonitrile (10 ml). The solution turned dark green and was stirred overnight at room temperature. Ferrocenium hexafluorophosphate (693 mg, 2.1 mmol) was then added to the mixture in one portion, and after 1 h, the solids were removed by vacuum filtration. The filtrate was then concentrated to 5 ml, layered with diethyl ether (10 ml) and cooled to 243 K. After 3 d, (I) had formed as dark-red crystals. Cutting these large crystals produced smaller fragments which were suitable for X-ray analysis.

Crystal data

$[Co_3(C_{10}H_{21}N_2S)_3]Cl(PF_6)_2$
$M_r = 1106.22$
Monoclinic, $P2_1/n$
$a = 12.5020$ (2) Å
$b = 17.2040$ (3) Å
$c = 21.3400$ (3) Å
$\beta = 93.0940$ (11)°
$V = 4583.21$ (13) Å^3
$Z = 4$
$D_x = 1.603$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1038 reflections
$\theta = 1.9$–27.5°
$\mu = 1.42$ mm^{-1}
$T = 130$ (2) K
Prism, dark red
0.37 × 0.30 × 0.25 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.622$, $T_{max} = 0.718$
17 828 measured reflections
10 034 independent reflections
7664 reflections with $I > 2\sigma(I)$
$R_{int} = 0.036$
$\theta_{max} = 27.5°$
$h = -16 \rightarrow 16$
$k = -20 \rightarrow 22$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.104$
$S = 1.01$
10 034 reflections
530 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 1.2602P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.88$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0009 (2)

Table 1
Selected geometric parameters (Å, °).

N1—Co1	2.064 (2)	S2—Co2	2.2723 (7)
N2—Co1	2.084 (2)	S2—Co3	2.3128 (7)
N3—Co2	2.064 (2)	S3—Co3	2.2676 (7)
N4—Co2	2.081 (2)	S3—Co1	2.3237 (7)
N5—Co3	2.063 (2)	Cl1···Co1	2.6264 (7)
N6—Co3	2.095 (2)	Cl1···Co3	2.6535 (7)
S1—Co1	2.2593 (7)	Cl1···Co2	2.7143 (7)
S1—Co2	2.3152 (7)		
N1—Co1—N2	95.38 (9)	N3—Co2—S1	111.32 (6)
N1—Co1—S1	83.07 (6)	N4—Co2—S1	104.78 (6)
N2—Co1—S1	118.44 (7)	S2—Co2—S1	132.79 (3)
N1—Co1—S3	108.87 (6)	N5—Co3—N6	94.70 (8)
N2—Co1—S3	108.42 (7)	N5—Co3—S3	82.87 (6)
S1—Co1—S3	130.36 (3)	N6—Co3—S3	120.73 (7)
N3—Co2—N4	96.22 (8)	N5—Co3—S2	110.67 (6)
N3—Co2—S2	83.23 (6)	N6—Co3—S2	101.64 (7)
N4—Co2—S2	118.43 (6)	S3—Co3—S2	134.68 (3)

All H atoms were allowed for using a riding model, with C—H distances of 0.98 and 0.99 Å.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *maXus* (MacKay *et al.*, 1998) and *ZORTEP* (Zsolnai & Huttner, 1994).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1019). Services for accessing these data are described at the back of the journal.

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