Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Bis(μ-cystamine-$\kappa^4N,S:S',N'$)bis[(2-aminoethanethiolato-κ^2N,S)iridium(III)] tetrabromide dihydrate

Mitsuharu Fujita, Yoshitaro Miyashita,* Nagina Amir, Yasunori Yamada, Kiyoshi Fujisawa and Ken-ichi Okamoto

Department of Chemistry, University of Tsukuba, Tsukuba 305-8571, Japan
Correspondence e-mail: ymiya@chem.tsukuba.ac.jp

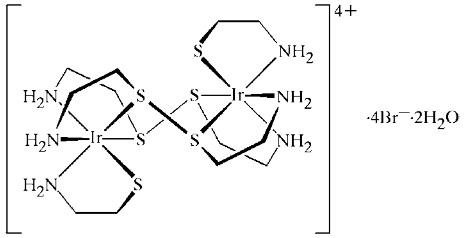
Received 3 June 2004
Accepted 9 July 2004
Online 11 August 2004

In the complex cation of the title compound, $[Ir_2(C_2H_6NS)_2(C_4H_{12}N_2S_2)_2]Br_4\cdot2H_2O$, which was obtained by rearrangement of $[Re\{Ir(aet)_3\}_2]^{3+}$ (aet is 2-aminoethanethiolate) in an aqueous solution, two approximately octahedral *fac*(*S*)-$[Ir(NH_2CH_2CH_2S)_3]$ units are linked by two coordinated disulfide bonds. The complex cation has a twofold axis, and the two non-bridging thiolate S atoms in the complex are located on opposite sides of the two disulfide bonds. Considering the absolute configurations of the two octahedral units (Δ and Λ) and the four asymmetric disulfide S atoms (*R* and *S*), the complex consists of the $\Delta_{RR}\Delta_{RR}$ and $\Lambda_{SS}\Lambda_{SS}$ isomers, which combine to form the racemic compound.

Comment

Previously, we have reported dinuclear Rh^{III} and Ir^{III} complexes containing a coordinated disulfide bond, *viz.* $[\{M(aet)_2\}_2(\mu\text{-cysta})]^{2+}$ (M = Rh^{III} and Ir^{III}, aet is 2-aminoethanethiolate and cysta is cystamine), which were formed by oxidation of mononuclear complexes containing three thiolate S atoms, *fac*(*S*)-$[M(aet)_3]$ (Konno *et al.*, 1997; Miyashita *et al.*, 1998). Furthermore, since thiolate S atoms can bridge two metal ions, construction of S-bridged polynuclear complexes using *fac*(*S*)-$[M(aet)_3]$ units as building blocks has been investigated (Konno, 2004). For example, the reaction of *fac*(*S*)-$[M(aet)_3]$ with metal ions which prefer an octahedral geometry, selectively forms linear-type trinuclear complexes, $[M'\{M(aet)_3\}_2]^{3+}$ (M' = Cr^{III}, Co^{III}, Rh^{III}, *etc.*; Mahboob *et al.*, 2004). Recently, we have synthesized the trinuclear complex involving the Re^{III} ion, *viz.* $[Re\{Ir(aet)_3\}_2]^{3+}$ (Mahboob *et al.*, 2002). During the course of the recrystallization processes, a novel dinuclear Ir^{III} complex containing two coordinated disulfide bonds was obtained. We report here the crystal structure of the title compound, $[\{Ir(aet)\}_2(\mu\text{-cysta})_2]Br_4\cdot2H_2O$, (I), for comparison with those of related complexes.

The asymmetric unit of (I) comprises one-half of a tetravalent dinuclear complex cation, two bromide anions and one water molecule. The complex cation consists of two approximately octahedral *fac*(*S*)-$[Ir(NH_2CH_2CH_2S)_3]$ units, which are linked by two disulfide bonds (Fig. 1). There is a crystallographic twofold axis through the center of the S1—S1^i and S2—S2^i bonds [symmetry code: (i) $1 - x, \frac{1}{2} - y, z$]. The two non-bridging thiolate S atoms (S3 and S3^i) are located on opposite sides of the two disulfide bonds. Considering the absolute configurations of the two octahedral units (Δ or Λ) and the four asymmetric disulfide S atoms (*R* or *S*), the present crystal of (I) is racemic, with $\Delta_{RR}\Delta_{RR}$ and $\Lambda_{SS}\Lambda_{SS}$ configurations. (The isomer shown in Fig. 1 is the $\Lambda_{SS}\Lambda_{SS}$ isomer.) This configuration contrasts with the fact that the corresponding single disulfide-bridged complexes $[\{M(aet)_2\}_2(\mu\text{-cysta})]^{2+}$ (M = Rh^{III} and Ir^{III}) are selectively obtained as the *meso* isomer, with $\Delta_R\Lambda_S$ configurations (Konno *et al.*, 1997; Miyashita *et al.*, 1998). On the other hand, a triple disulfide-bridged Ru^{III} complex (Albela *et al.*, 1999) and a triple diselenide-bridged Rh^{III} complex (Konno *et al.*, 2003) are obtained as the racemic isomer with $\Delta_{RRR}\Delta_{RRR}$ and $\Lambda_{SSS}\Lambda_{SSS}$ configurations.



(I)

In (I), the Ir—N(*trans* to disulfide) distances [mean 2.089 (12) Å] are shorter than the Ir—N(*trans* to thiolate) distances [2.148 (10) Å; Table 1]. This behavior is in agreement with the case of $[\{Ir(aet)_2\}_2(\mu\text{-cysta})]^{2+}$ (Konno *et al.*, 1997; Miyashita *et al.*, 1998), implying the *trans* influence of thiolate S atoms. The Ir—S(disulfide) distances in (I) [mean 2.304 (3) Å] are *ca* 0.04 Å shorter than the Ir—S(thiolate) distances [2.348 (3) Å]. The difference between these distances is smaller than that (0.08 Å) in $[\{Ir(aet)_2\}_2(\mu\text{-cysta})]^{2+}$, probably because the S—S distances [mean 2.127 (6) Å] in (I) are slightly shorter than that [2.158 (3) Å] in

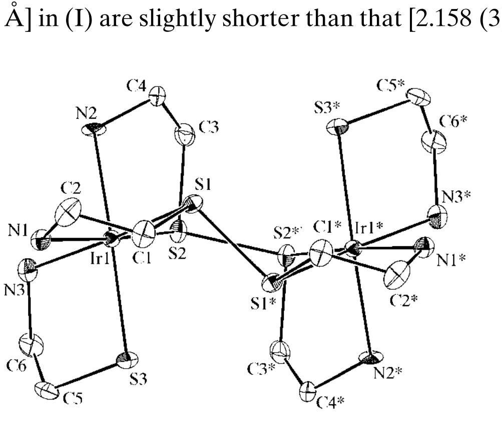


Figure 1
A perspective drawing of the $\Lambda_{SS}\Lambda_{SS}$ isomer of $[\{Ir(aet)\}_2(\mu\text{-cysta})_2]^{4+}$, with the atom-numbering scheme, viewed down the crystallographic C_2 axis. Displacement ellipsoids are shown at the 30% probability level and H atoms have been omitted for clarity. Atoms labelled with an asterisk (*) are at the symmetry position $(1 - x, \frac{1}{2} - y, z)$.

DOI: 10.1107/S0108270104016816

[{Ir(aet)$_2$}$_2$(μ-cysta)]$^{2+}$. In addition, these S—S distances are relatively long. For example, the S—S distance in [{IrCl(μ-SC$_6$H$_2$Me$_2$CH$_2$)(PPh$_3$)}$_2$(μ-ArSSAr)] (Ar is mesityl) is 2.109 (3) Å (Matsukawa *et al.*, 2000).

Since the S(disulfide)—Ir—S(disulfide) angles [100.3 (1)°] are significantly larger than the ideal angle (90°), the N(*trans* to disulfide)—Ir—N(*trans* to disulfide) angles [86.9 (5)°] are smaller than the other N—Ir—N angles. On the other hand, the S(disulfide)—Ir—S(disulfide) angle in (I) is smaller than those in [M_2LI_2(MeCN)$_2$]$^{2+}$ [mean 110.80 (4)° for M = Cu^{II} and mean 110.5 (2)° for M = Ni^{II}] with a macrocyclic ligand L (Fox *et al.*, 2000). Therefore, the stereochemistry of the complex cation in (I) shows less strain, *i.e.* the Ir—S—S—Ir torsion angles deviate from 0°. Interestingly, the two disulfide bonds have obviously distinguishable torsion angles (Table 1). Atom N1 of the aet moiety involving atom S1 occupies the position *trans* to the disulfide S atom, whereas atom N2 of the aet moiety involving atom S2 occupies the position *trans* to the thiolate S atom. This difference leads to the difference in bond angles involving the disulfide bonds.

Since (I) could not be obtained by the direct oxidation of Δ/Λ-*fac*(*S*)-[Ir(aet)$_3$] or $\Delta_R\Lambda_S$-[{Ir(aet)$_2$}$_2$(μ-cysta)]$^{2+}$, it appears that the absolute configuration plays an important role in the formation of dinuclear complexes.

Experimental

Orange powder of ΔΔ/ΛΛ-[Re{Ir(aet)$_3$}$_2$]I$_3$ (Mahboob *et al.*, 2002) was dissolved in a small amount of water and subjected to a QAE Sephadex A-25 column (Br$^-$ form). The orange solution, which was eluted with water, was concentrated on a rotary evaporator and kept in a refrigerator after the addition of a few drops of a saturated NaBr aqueous solution. A small number of orange octahedral crystals appeared within several days.

Crystal data

[Ir$_2$(C$_2$H$_6$NS)$_2$(C$_4$H$_{12}$N$_2$S$_2$)$_2$]Br$_4$·2H$_2$O
M_r = 1196.90
Tetragonal, $I4_1/a$
a = 16.392 (3) Å
c = 22.784 (6) Å
V = 6121 (2) Å^3
Z = 8
D_x = 2.597 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 22 reflections
θ = 10.0–12.8°
μ = 14.38 mm^{-1}
T = 296.2 K
Octahedron, red
0.15 × 0.15 × 0.15 mm

Data collection

Rigaku AFC-7S diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min}$ = 0.102, $T_{\max}$ = 0.116
4032 measured reflections
3512 independent reflections
2082 reflections with $F^2 > 2\sigma(F^2)$
$R_{\rm int}$ = 0.044
$\theta_{\max}$ = 27.5°
$h = -6 \rightarrow 21$
$k = 0 \rightarrow 21$
$l = -8 \rightarrow 29$
3 standard reflections every 150 reflections intensity decay: 9.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.117
S = 1.01
3512 reflections
145 parameters
H-atom parameters constrained
$w = 1/(\sigma^2(F_o^2) + \{0.03[\mathrm{Max}(F_o^2,0) + 2F_c^2]/3\}^2)$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 1.72 e Å^{-3}
$\Delta\rho_{\min}$ = −1.93 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ir1—S1	2.313 (3)	Ir1—N2	2.148 (10)
Ir1—S2	2.295 (3)	Ir1—N3	2.096 (12)
Ir1—S3	2.348 (3)	S1—S1^{i}	2.130 (6)
Ir1—N1	2.082 (11)	S2—S2^{i}	2.124 (6)
S1—Ir1—S2	100.3 (1)	N1—Ir1—N3	86.9 (5)
S1—Ir1—S3	94.9 (1)	N2—Ir1—N3	91.4 (4)
S2—Ir1—S3	96.6 (1)	Ir1—S1—S1^{i}	106.3 (2)
N1—Ir1—N2	94.3 (4)	Ir1—S2—S2^{i}	121.96 (9)
Ir1—S1—S1^{i}—Ir1^{i}	88.7 (2)	C1—S1—S1^{i}—C1^{i}	−71.3 (10)
Ir1—S2—S2^{i}—Ir1^{i}	−24.5 (4)	C3—S2—S2^{i}—C3^{i}	−163.3 (10)

Symmetry code: (i) $1 - x, \frac{1}{2} - y, z$.

H atoms bonded to C or N atoms were positioned geometrically and allowed to ride on their attached atoms [C—H = N—H = 0.95 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N)]. H atoms of water molecules were not included in the calculations.

Data collection: *WinAFC Diffractometer Control Software* (Rigaku, 1999); cell refinement: *WinAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

This work was supported by Grants-in-Aid for Scientific Research and the COE program of the Japan Society for the Promotion of Science.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1185). Services for accessing these data are described at the back of the journal.

References

Albela, B., Bothe, E., Brosch, O., Mochizuki, K., Weyhermüller, T. & Wieghardt, K. (1999). *Inorg. Chem.* **38**, 5131–5138.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, M., Giacovazzo, C., Guagliardi, A. & Polidori, G. (1994). *J. Appl. Cryst.* **27**, 435.
Fox, S., Stibrany, R. T., Potenza, J. A., Knapp, S. & Schugar, H. J. (2000). *Inorg. Chem.* **39**, 4950–4961.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Konno, T. (2004). *Bull. Chem. Soc. Jpn*, **77**, 627–649.
Konno, T., Haneishi, K., Hirotsu, M., Yamaguchi, T., Ito, T. & Yoshimura, T. (2003). *J. Am. Chem. Soc.* **125**, 9244–9245.
Konno, T., Miyashita, Y. & Okamoto, K. (1997). *Chem. Lett.* pp. 85–86.
Mahboob, N., Miyashita, Y., Yamada, Y., Fujisawa, K. & Okamoto, K. (2002). *Polyhedron*, **21**, 1809–1816.
Mahboob, N., Miyashita, Y., Yamada, Y., Fujisawa, K. & Okamoto, K. (2004). *Inorg. Chim. Acta*, **357**, 75–82.
Matsukawa, S., Kuwata, S. & Hidai, M. (2000). *Inorg. Chem.* **39**, 791–798.
Miyashita, Y., Sakagami, N., Yamada, Y., Konno, T. & Okamoto, K. (1998). *Bull. Chem. Soc. Jpn*, **71**, 2153–2160.
Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10b. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Rigaku (1999). *WinAFC Diffractometer Control Software.* Version 1.0.2. Rigaku Corporation, 3–9–2 Akishima, Tokyo, Japan.