Preparation and Structure of *syn*- and *anti*-Bis(μ-thioacetato-κ^2S)bis[bis(dithioacetato-κS:κS′)-iridium(III)]

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Iridium(III) dinuclear complexes with thioacetato bridges and dithioacetato chelates were prepared by the reaction of $H_2IrCl_6 \cdot 6H_2O$ with a mixture of Li_2CO_3, MeCOSH, $MeCO_2H$, and $(MeCO)_2O$ under O_2. X-ray structures of two geometrical isomers for $[\{Ir(S_2CMe)_2\}_2(\mu\text{-}SOCMe)_2]$ were determined.

Monothiocarboxylates are interesting ligands because they show various coordination modes; monodentate, chelate, and bridging.[1,2] We have tried to synthesize M–M bonded iridium(II) dinuclear complexes with thioacetato bridges in an analogous reaction condition to that for $[Ir_2(\mu\text{-}O_2CMe)_2Cl_2(CO)_2]$.[3] Unexpectedly, the reaction products were an edge-sharing bioctahedral iridium(III) dinuclear complex, *anti*-$[\{Ir(S_2CMe)_2\}_2(\mu\text{-}SOCMe)_2]$ (**1a**), and a mononuclear iridium(III) complex, $[Ir(S_2CMe)_3]$ (**2**), both of which have dithioacetato ligands. A similar conversion of monothiocarboxylate to dithiocarboxylate was reported in the synthesis of $[Ni(S_2CPh)_2]$ complex of which $PhCS_2^-$ was formed by disproportionation of $PhCSO^-$.[4]

The ^{1}H NMR spectrum of compound **1a** in $CDCl_3$ showed 2:1 intensity peaks at 2.633 and 2.401 ppm at 20 °C. When the solution of **1a** was left for 24 h under room light, the NMR spectrum gave a pair of new peaks at 2.629 and 2.238 ppm (intensity ratio, 2:1) of which relative intensity to **1a** was about 0.8 and many weak intensity peaks between 2 and 3 ppm also appeared. Because the spectrum of **1a** does not change in the dark, this reaction must include a photochemical process. The GPC (gel permeation chromatography) separation of the products in an irradiated solution of **1a** with 1,2-dichloromethane as the eluent gave three bands. The first band is a geometrical isomer of **1a**, *syn*-$[\{Ir(S_2CMe)_2\}_2(\mu\text{-}SOCMe)_2]$ (**1b**), and the third one is compound **1a**. The second band includes the unknown products which have many peaks between 2 and 3 ppm in the ^{1}H NMR spectra. Their yields were too low for identification. In $CDCl_3$, the isomer **1b** also transformed to a mixture of **1a**, **1b**, and some uncharacterized products under room light.

Complexes **1a** and **1b** are edge-sharing bioctahedra with four chelating dithioacetato and two bridging thioacetato ligands. Complexes **1a** and **1b** take *anti*- and *syn*-geometries, respectively, in the mutual arrangement of the MeCO moieties. Although *syn*- and *anti*-isomers are possible for all complexes with an $M_2(\mu\text{-}SR)_2$ unit, only for $[\{Re(CO)_2Cl(NO)\}_2(\mu\text{-}SCMe_3)_2]$ have the structures of both of the isomers been reported. They were obtained as crystals that have both *syn*- and *anti*-isomers in a unit cell.[5]

The structures of **1a** and **1b** are shown in Fig. 1. Both of them have two bridging thioacetato in which S atoms are bound to the iridium atoms. The bond-lengths of O–C (**1a**; 1.197(13) and **1b**; 1.170(12) and 1.201(10) Å) and S–C (**1a**; 1.814(10) and **1b**; 1.850(10) and 1.839(9) Å) suggest that these are C=O and C–S, respectively. This type of monothiocarboxylato bridge has been reported for several complexes.[2,6–8] The remaining coordination sites are occupied by dithioacetato chelate ligands. Compound **1a** has an inversion center and **1b** has a pseudo-2-fold axis, and the configuration around each iridium atom is ΔΛ for **1a** and ΔΔ or ΛΛ for **1b**. The *syn*-orientation for the ΔΛ configuration and the *anti* for the ΔΔ or ΛΛ may be more strained than the configurations of **1a** and **1b**, respectively. The geometry around each Ir atom in **1a** is a slightly distorted octahedron with six sulfur atoms. Any close contacts between the acetyl groups of the thioacetato ligands and the chelating dithioacetato ligands are not observed in the structure of **1a**. The structure of **1b** is more distorted than that of **1a**. In the structure of **1b**, the oxygen and the methyl carbon atoms of the thioacetato ligands have close contact with the S and the carboxy carbon atoms of dithioacetato ligands (O1···S10 2.931(11), O2···S4 2.870(9), C6···C3 3.457(16), and C8···C11 3.387(17) Å). It is interesting that the reversible conversion between these less and more crowded structures occurs photochemically.

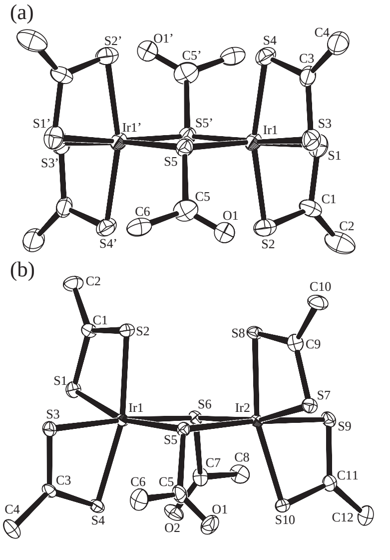

Fig. 1. ORTEP diagrams with the 30% probability ellipsoids. (a) **1a**. Selected bond distances (Å): Ir1–S1 2.352(2), Ir1–S2 2.362(2), Ir1–S3 2.330(2), Ir1–S4 2.367(2), Ir1–S5 2.363(2), Ir1–S5′ 2.382(2). (b) **1b**. Selected bond distances (Å): Ir1–S1 2.355(2), Ir1–S2 2.365(2), Ir1–S3 2.364(2), Ir1–S4 2.369(2), Ir1–S5 2.393(2), Ir1–S6 2.357(2), Ir2–S5 2.368(2), Ir2–S6 2.387(2), Ir2–S7 2.345(2), Ir2–S8 2.373(2), Ir2–S9 2.369(2), Ir2–S10 2.363(2).

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Compound **2** is a normal tris chelate type structure. The iridium atom lies on the crystallographic 2-fold axis. The geometry of the IrS_6 unit is quite similar to that in tris(dithiocarbamato)iridium(III) complexes.[9–11]

Experimental

General. All reagents were obtained from commercial sources and used as received. A preparative GPC separation with 1,2-dichloroethane eluent was done by using a Japan Analytical Industry LC-908 with JAIGEL-H columns. ^1H NMR spectra were measured on a JEOL α-400 spectrometer. IR spectra were measured on a Perkin-Elmer 1600 series FT-IR spectrophotometer.

Synthesis of 1a and 2. A solution of $H_2IrCl_6 \cdot 6H_2O$ (503 mg, 0.977 mmol) and Li_2CO_3 (145 mg, 1.96 mmol) in a mixture of MeCOSH (4 mL), $MeCO_2H$ (4 mL), and $(MeCO)_2O$ (4 mL) was refluxed for 1 h with bubbling O_2 gas. The resulting orange precipitate of **1a** was filtered, rinsed with diethyl ether (2 mL × 5) and acetonitrile (2 mL × 10), and dried under vacuum (yield 0.061 g, 14%). The dark-red crystals of **2** were deposited from the filtrate on standing. The crystals were filtered, washed with diethyl ether (2 mL × 10), and dried under vacuum (yield 0.161 g, 35%). **1a**: Calcd for $C_6H_9IrOS_5$: C, 16.03; H, 2.02%. Found: C, 15.99; H, 1.85%. ^1H NMR ($CDCl_3$): δ 2.633 (s, 12H, S_2CMe), 2.401 (s, 6H, SOC*Me*). IR (KBr): 1694 (s), 1418 (m), 1347 (m), 1190 (s), 1141 (s), 1109 (s), 947 (m), 841 (s), 608 (s) cm^{-1}. **2**: Calcd for $C_6H_9IrS_6$: C, 15.47; H, 1.95%. Found: C, 15.46; H, 1.90%. ^1H NMR ($CDCl_3$): δ 2.65 (s, 12H). IR (KBr): 1188 (s), 1134 (s), 837 (s) cm^{-1}.

Synthesis of 1b. A benzene solution (10 mL) of **1a** (10 mg) was left at room temperature for 2 days under room light. The orange solid obtained by evaporation of the solution was dissolved in 10 mL of 1,2-dichloroethane and filtered. The sample was separated into three components by recycling the solution in the columns with the preparative GPC equipment. The third band was collected and evaporated to dryness (yield 5.6 mg, 56%). ^1H NMR ($CDCl_3$): δ 2.629 (s, 12H, S_2CMe), 2.238 (s, 6H, SOC*Me*). IR (KBr pellet): 1697 (s), 1421 (m), 1345 (m), 1189 (s), 1140 (s), 1105 (s), 947 (m), 840 (s), 604 (s) cm^{-1}.

X-ray Crystallography. Crystals of **1a** were obtained directly from the reaction solution. Crystals of **1b** were given by the slow diffusion of *n*-hexane to a diethyl ether solution at −24 °C. **2** was crystallized by the slow evaporation of a diethyl ether solution. All measurements were carried out on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). The data were collected using the ω–2θ scan technique to a maximum 2θ value of 55°. All calculations were performed by using teXsan. Scattering factors for neutral atoms were from Cromer and Waber[12] and anomalous dispersion[13] was included. The structures were solved by direct methods, SHELXS86.[14] An analytical absorption correction[15] was applied. Crystal data of **1a**: $C_{12}H_{18}Ir_2O_2S_{10}$; MW 899.31; triclinic; space group $P\bar{1}$ (No. 2); $a = 7.2432(9)$ Å; $b = 9.751(2)$ Å; $c = 10.385(2)$ Å; $\alpha = 110.78(1)^\circ$; $\beta = 95.94(1)^\circ$; $\gamma = 111.04(1)^\circ$; $V = 617.2(2)$ Å^3; $Z = 1$; $D_{calcd} = 2.419\ g\,cm^{-3}$; $\mu(\text{Mo K}\alpha) = 11.65\ mm^{-1}$; $T = 23\ ^\circ C$; reflection with $I > 2\sigma(I)$ 2371; $R_1(F_o)$, 0.039; $R_w(F_o{}^2)$, 0.105. Crystal data of **1b**: $C_{12}H_{18}Ir_2O_2S_{10}$; MW 899.31; monoclinic; space group $P2_1/c$ (No. 14); $a = 15.958(1)$ Å; $b = 8.738(1)$ Å; $c = 17.335(2)$ Å; $\beta = 90.475(8)^\circ$; $V = 2417.1(4)$ Å^3; $Z = 4$; $D_{calcd} = 2.471\ g\,cm^{-3}$; $\mu(\text{Mo K}\alpha) = 11.90\ mm^{-1}$; $T = -76\ ^\circ C$; reflection with $I > 2\sigma(I)$ 3940; $R_1(F_o)$, 0.040; $R_w(F_o{}^2)$, 0.087. Crystal data of **2**: $C_{12}H_{18}Ir_2S_{12}$; MW 465.72; orthorhombic; space group *Pbcn* (No. 60); $a = 11.647(1)$ Å; $b = 9.363(1)$ Å; $c = 11.945(2)$ Å; $V = 1302.6(3)$ Å^3; $Z = 4$; $D_{calcd} = 2.375\ g\,cm^{-3}$; $\mu(\text{Mo K}\alpha) = 11.20\ mm^{-1}$; $T = 23\ ^\circ C$; reflection with $I > 2\sigma(I)$ 817; $R_1(F_o)$, 0.034; $R_w(F_o{}^2)$, 0.087. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC276378–276380 for compound Nos. **1a**, **1b**, and **2**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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