Bromide ion binding by a dinuclear gold(I) *N*-heterocyclic carbene complex: A spectrofluorescence and X-ray absorption spectroscopic study

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Electronic Supplementary Information

Contents

Table S1 Constraints and restraints used in the MS EXAFS analysis of **1**.$(PF_6)_2$ in DMSO.

Mean displacement factor constraints (Å^2)	$\sigma^2_{(C1)} = \sigma^2_{(C2)}$ $\sigma^2_{(N4)} = \sigma^2_{(N5)} = \sigma^2_{(N6)} = \sigma^2_{(N7)}$ $\sigma^2_{(C8)} = \sigma^2_{(C9)} = \sigma^2_{(C10)} = \sigma^2_{(C11)}$
Mean displacement factor restraints (Å^2)	$\sigma^2_i > 0.0005 \ \{0.0001\}$ where i is all shells $\sigma^2_i < 0.02 \ \{0.01\}$ where i is all shells
Bond length restraints (Å)	C(1) – Au(0) ~= 2.03 {0.05} C(2) – Au(0) ~= 2.03 {0.05} C(1) – N(5) ~= 1.38 {0.05} C(5) – C(9) ~= 1.40 {0.05} C(8) – C(9) ~= 1.35 {0.05} C(8) – N(4) ~= 1.40 {0.05} N(4) – C(1) ~= 1.38 {0.05} C(2) – N(6) ~= 1.38 {0.05} N(6) – C(11) ~= 1.40 {0.05} C(10) – C(11) ~= 1.35 {0.05} C(10) – N(7) ~= 1.40 {0.05} N(7) – C(2) ~= 1.38 {0.05}
Bond angle restraints (°)	Au(0) – C(1) – N(5) ~= 127 {5} Au(0) – C(1) – N(4) ~= 127 {5} C(1) – N(5) – C(9) ~= 110 {5} N(5) – C(1) – N(4) ~= 106 {5} N(5) – C(9) – C(8) ~= 107 {5} C(9) – C(8) – N(4) ~= 107 {5} C(8) – N(4) – C(1) ~= 110 {5} Au(0) – C(2) – N(6) ~= 127 {5} Au(0) – C(2) – N(6) ~= 127 {5} C(2) – N(6) – C(11) – N(6) ~= 110 {5} N(6) – C(2) – N(7) ~= 106 {5} N(6) – C(11) – C(10) ~= 107 {5} C(11) – C(10) – N(7) ~= 107 {5} C(10) – N(7) – C(2) ~= 110 {5}
Symmetry restraints	$zi = 0$, where i is all shells except Au(3) xAu(3) = 0 yAu(3) = 0 xN(4) = xN(5) xN(6) = xN(7) xC(8) = xC(9) xC(10) = xC(11) xC(1) = -xC(2) xN(4) = -xN(7) xN(5) = -xN(6) xC(8) = -xC(10) xC(9) = -x(11) yC(1) = yC(2) yN(4) = -yN(5) yN(6) = -yN(7) yC(8) = -yC(9) yC(10) = -yC(11) yN(6) = yN(5) yN(7) = yN(4) yC(10) = yC(8) yC(11) = yC(9)
Occupancy (N) restraints	$N_i = 1$, where i is all shells

XFit Data Analysis – Determinacy, Goodness-of-Fit and Monte-Carlo Error Analysis

Determinacy

The number of parameters being fitted, p, compared to the number of independent information data points (independent points in the EXAFS plus the number of independent structural parameters), N_i, was calculated to give the degree of determinacy N_i/p. If this ratio is < 1, then the model is considered to be underdetermined and a unique fit is not possible. In all cases the ratio was > 1 and, hence, the models were overdetermined. The value of N_i is given by:[1]

$$N_i = 2(\Delta r)(\Delta k)/\pi + \Sigma[D(N-2)+1] \qquad (1)$$

where D is the number of dimensions in which the refinement takes place and N is the number of atoms in the unit.[2]

Goodness-of-Fit (Residual)

The method of determining the goodness of fit was through an R value where R is given by:

$$R = (\chi^2/\chi^2_{calculated=0})^{1/2} \qquad (2)$$

where χ^2 is the quantity minimized during the refinement and $\chi^2_{calculated=0}$ is the value of χ^2 when the calculated EXAFS is uniformly 0.[3] Residual R values of $\leq 20\%$ were considered reasonable for MS models, and relatively high ($>20\%$) values of R are explained by the exclusion of multiple-scattering contributions on the SS models.[2, 4]
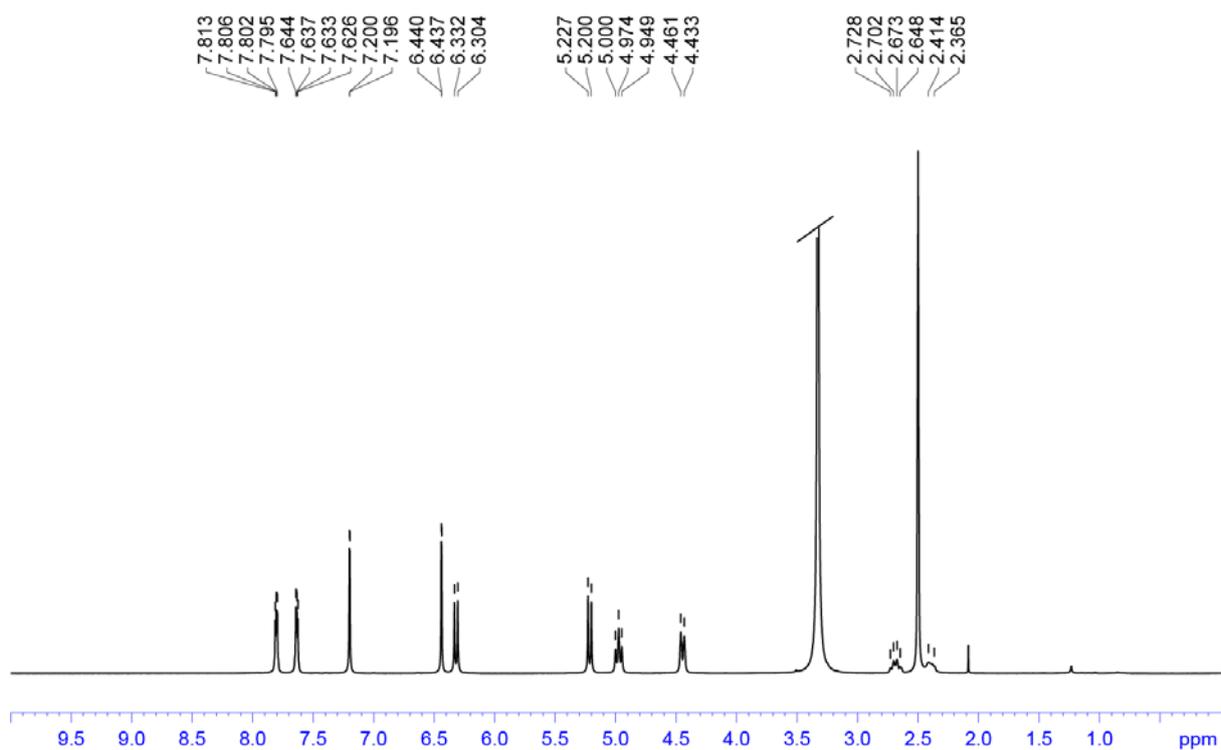
Monte-Carlo Error Analysis

Monte Carlo analyses were conducted to estimate the rms deviations in final parameters arising from the noise in the data. Two consecutive sets of 16×16 Monte-Carlo cycles were calculated and the resulting rms errors were combined with systematic errors to determine the final error estimates. The probable errors in the Au-C and Au•••Au bond lengths were estimated as $[\sigma_r^2 + \sigma_s^2]^{1/2}$, where σ_r and σ_s represent contributions from the random and systematic errors, respectively. The random (statistical) errors due to noise in the data were estimated by Monte Carlo calculations,[3] and the systematic errors were assigned a conservative consensus value, 0.02 Å.[5]

The following applies to tables of multiple scattering pathways presented in the supporting information: [a]The number of legs represents the path travelled by the photoelectron originating from and returning to the XAFS absorber Au(0). [b]The total distance travelled by the photoelectron (R_{eff}) is twice the value of R_{as}. [c]The importance factor (given to 2 d.p.), represents the percent contribution of a path relative to the strongest path Au(0) → C(1) → Au(0), including contribution from the Debye-Waller Factors. All pathways have a maximum of 5 legs per MS pathway, curve and plane wave filters of 3% and 2%, respectively, $R_{eff} \leq 10$ Å.

Table S2 Paths and importance factors from MS analysis (Table 1), for the MS refinement of the EXAFS of **1**.$(PF_6)_2$.

Atoms in MS Pathway	Legs[a]	Deg	R_{as} (Å)[b]	Importance Factor[c]
Au(0) →C(1) →Au(0)	2	2	2.03	100.00%
Au(0) →Au(3) →Au(0)	2	1	3.02	20.45%
Au(0) →N(4) →Au(0)	2	4	3.06	100.00%
Au(0) →N(6) →C(2) →Au(0)	3	8	3.23	100.00%
Au(0) →C(2) →N(6) →C(2) →Au(0)	4	4	3.40	30.40%
Au(0) →C(2) →C(1) →Au(0)	3	2	4.06	17.00%
Au(0) →C(1) →Au(0) →C(2) →Au(0)	4	2	4.06	32.47%
Au(0) →C(1) →Au(0) →C(1) →Au(0)	4	2	4.06	9.57%
Au(0) →N(4) →N(5) →Au(0)	3	4	4.16	6.03%
Au(0) →C(10) →Au(0)	2	4	4.25	28.73%
Au(0) →C(9) →C(1) →Au(0)	3	8	4.28	64.64%
Au(0) →C(2) →N(6) →N(7) →Au(0)	4	8	4.33	21.17%
Au(0) →C(1) →C(9) →C(1)	3	4	4.30	42.92%
Au(0) →C(10) →N(7) →Au(0)	3	8	4.36	43.09%
Au(0) →N(4) →C(8) →C(1) →Au(0)	4	8	4.38	55.71%
Au(0) →N(7) →C(2) →N(7) →Au(0)	4	4	4.43	24.06%
Au(0) →N(5) →C(1) →N(4) →Au(0)	4	4	4.43	5.63%
Au(0) →C(1) →N(4) →N(5) →C(1) →Au(0)	5	4	4.50	11.14%
Au(0) →N(6) →C(11) →N(6) →Au(0)	4	4	4.46	22.57%
Au(0) →C(8) →N(4) →C(1) →Au(0)	4	8	4.53	39.22%
Au(0) →C(1) →C(9) →N(5) →C(1) →Au(0)	5	8	4.55	41.91%
Au(0) →C(1) →N(4) →C(1) →N(5) →Au(0)	5	8	4.60	12.52%
Au(0) →N(4) →C(1) →N(4) →C(1) →Au(0)	5	8	4.60	28.98%
Au(0) →N(5) →C(9) →N(5) →C(1) →Au(0)	5	8	4.63	36.46%
Au(0) →C(9) →N(4) →Au(0)	3	8	4.77	9.88%
Au(0) →C(2) →C(11) →N(7) →Au(0)	4	8	4.79	10.43%
Au(0) →N(7) →C(10) →N(6) →Au(0)	4	8	4.87	4.55%
Au(0) →C(9) →C(8) →Au(0)	3	4	4.92	5.45%
Au(0) →C(8) →N(5) →C(1) →Au(0)	4	8	4.94	11.53%
Au(0) →C(11) →C(10) →C(2) →Au(0)	4	8	4.95	13.32%

[1](PF$_6$)$_2$

Peak labels (ppm): 7.813, 7.806, 7.802, 7.795, 7.644, 7.637, 7.633, 7.626, 7.200, 7.196, 6.440, 6.437, 6.332, 6.304, 5.227, 5.200, 5.000, 4.974, 4.949, 4.461, 4.433, 2.728, 2.702, 2.673, 2.648, 2.414, 2.365

^{1}H NMR Spectrum of [**1**](PF$_6$)$_2$ in d6-DMSO

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