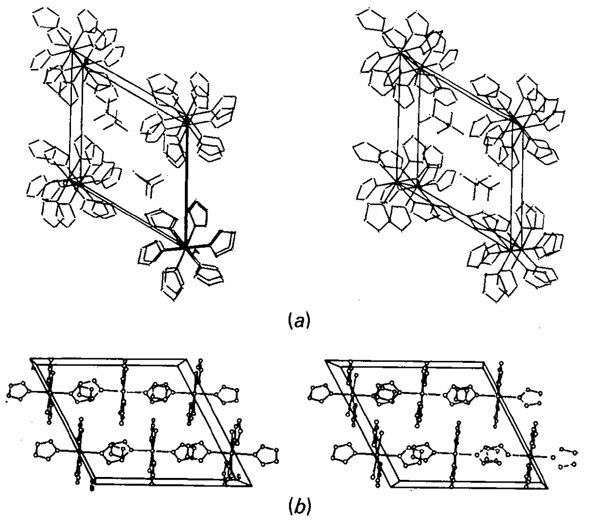

Fig. 2. Stereoscopic views of the crystal structures. (a) Compound (1) down **c**; (b) compound (2) down **b**.

dihedral angles are 89·1 (1) and 90·9 (1)°, respectively. This shows that the Cl atoms may take the apical positions in the coordination sphere more easily than the perchlorate anions.

The crystal structures are shown in Fig. 2. The structure of (1) is isostructural with that of hexakis(pyrazole)Ni^{II} nitrate (Reimann, Santoro & Mighell, 1970), whereas (2) is isostructural with the corresponding copper(II) (Mighell, Santoro, Prince & Reimann, 1975) and nickel(II) (Reimann, Mighell & Mauer, 1967) complexes. There are no contacts $X(-H)\cdots Y$, where $X=$ C or N and $Y=$ O or Cl, less than the sum of the van der Waals radii (Taylor & Kennard, 1982) in these crystal structures. Therefore there are no hydrogen bonds, but the structures are held together through weak van der Waals interactions.

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The Structure of $[Au\text{-}\mu\text{-}\{3,5\text{-}(C_6H_5)_2C_3HN_2\}]_3Cl_2$: a Trinuclear Mixed-Valence Gold Pyrazolate Complex

BY RAPHAEL G. RAPTIS, H. H. MURRAY AND JOHN P. FACKLER JR*

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, *USA*

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Abstract. Tris-μ-(3,5-diphenyl-1-pyrazolyl-N,N')-dichlorogold(III)digold(I), $M_r = 1319{\cdot}2$, monoclinic, $P2_1/c$, $a = 16{\cdot}477$ (3), $b = 9{\cdot}626$ (2), $c = 25{\cdot}686$ (4) Å, $\beta = 91{\cdot}16$ (1)°, $V = 4073$ (1) Å^3, $D_x = 2{\cdot}15$ Mg m^{-3}, $Z = 4$, $\mu = 10{\cdot}93$ mm^{-1}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $F(000) = 2464$, $T = 298$ K. The structure consists of a discrete trinuclear gold pyrazolate molecule containing a four-coordinate gold(III) center with *trans* chloride ligands and two two-coordinate gold(I) centers. The Au atoms are symmetrically bridged by the pyrazolate

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* To whom all correspondence should be addressed.

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anion ligands. The nine-membered heterocyclic ring of the complex is almost planar, with the metal-atom centers separated by distances of 3·334 (1)–3·383 (1) Å. Convergence to final conventional R values of $R = 0{\cdot}0443$ and $wR = 0{\cdot}0398$ was obtained using 208 variable parameters and 2703 reflections with $F_o^2 > 3\sigma(F_o^2)$.

Introduction. Our studies of dinuclear and trinuclear late transition metal complexes (Basil *et al.*, 1985; Murray, Briggs, Garzón, Raptis, Porter & Fackler, 1987) have led to the characterization of complexes containing gold in the I, II, III as well as mixed I/III oxidation states. The structural features of complexes containing gold in more than one oxidation state are of particular interest. We are focusing our efforts on understanding the two-electron oxidation of $\mathrm{Au^I/Au^I}$ dinuclear systems and the two-electron reduction of $\mathrm{Au^{III}/Au^{III}}$ systems. Both processes can lead to homovalent $\mathrm{Au^{II}/Au^{II}}$ complexes with formation of a metal–metal bond, or to mixed-valence $\mathrm{Au^I/Au^{III}}$ complexes.

Oxidative addition of halogens to the dinuclear $\mathrm{Au^I}$ ylide $[\mathrm{Au(CH_2)_2P(C_6H_5)_2}]_2$ gives, in a stepwise manner, the homovalent $\mathrm{Au^{II}}$, $[\mathrm{Au(CH_2)_2P(C_6H_5)_2}]_2X_2$, and $\mathrm{Au^{III}}$, $[\mathrm{Au(CH_2)_2P(C_6H_5)_2}]_2X_4$ species (Schmidbaur & Franke, 1975). Reductive elimination from the $\mathrm{Au^{III}}$ complex yields either the homovalent $\mathrm{Au^{II}}$ or the heterovalent $\mathrm{Au^I/Au^{III}}$ complex (Basil, 1983; Raptis, Porter, Murray & Fackler, 1988). The two-electron oxidative addition to the $\mathrm{Au^I}$ complex $[\mathrm{Au(CH_2)P(S)(C_6H_5)_2}]_2$ can also result in homo- or heterovalent products (Mazany & Fackler, 1984), the latter with concomitant rearrangement of the bridging ligand. The oxidation of the trinuclear complex $[\mathrm{Au}\text{-}\mu\text{-}\{3,5\text{-}(\mathrm{CH_3})_2\mathrm{C_3HN_2}\}]_3$ with $\mathrm{I_2}$ (Minghetti, Banditelli & Bonati, 1979) produced the heterovalent $\mathrm{Au^I_2/Au^{III}}$ species, as was suggested by its Mössbauer spectrum (Katada *et al.*, 1983).

Here we report the crystal structure of the mixed-valence trinuclear gold complex $[\mathrm{Au}\text{-}\mu\text{-}\{3,5\text{-}(\mathrm{C_6H_5})_2\mathrm{C_3HN_2}\}]_3\mathrm{Cl_2}$, obtained from the reaction of $\mathrm{AuCl_3(C_5H_5N)}$ and $\mathrm{Na}[3,5\text{-}(\mathrm{C_6H_5})_2\mathrm{C_3HN_2}]$.

Experimental. $\mathrm{AuCl_3(C_5H_5N)}$ was prepared following a literature procedure (Gibson & Colles, 1931). 3,5-Bis(phenyl)pyrazole was purchased from Fluka and deprotonated with sodium hydride. The trinuclear complex $[\mathrm{Au}\text{-}\mu\text{-}\{3,5\text{-}(\mathrm{C_6H_5})_2\mathrm{C_3HN_2}\}]_3\mathrm{Cl_2}$ was prepared by the addition of $\mathrm{Na}[3,5\text{-}(\mathrm{C_6H_5})_2\mathrm{C_3HN_2}]$ to an equimolar solution of $\mathrm{AuCl_3(C_5H_5N)}$ in tetrahydrofuran. Single crystals suitable for X-ray analysis were obtained by recrystallization from a tetrahydrofuran/diethyl ether solution.

Single multi-faceted red crystal of approximate dimensions 0·10 × 0·40 × 0·05 mm mounted in a random orientation on a glass fiber. Monoclinic symmetry suggested on the basis of interaxial angles and confirmed by a Delaunay reduction. Axial lengths checked by comparison with the interlayer spacings observed in axial photographs. Refined cell parameters obtained from the setting angles of 20 reflections with $20 < 2\theta < 30°$. Data collection carried out at room temperature using the ω scanning technique in bisecting geometry (Nicolet *R*3*m*/*E* diffractometer, graphite-monochromated Mo $K\alpha$ radiation). Intensities measured for 5934 unique reflections ($h < 18$, $k < 11$, $|l| < 28$) with $0 < 2\theta < 45°$, no symmetry-equivalent reflections were collected. Scan rate variable, 3–30° min^{-1}; scan range $-0{\cdot}8$ in ω from $K\alpha_1$ to $+0{\cdot}8$ from $K\alpha_2$. Backgrounds estimated from a 96-step peak profile. Three low-angle standards ($\bar{2}0\bar{6}$, $\bar{1}10$, $0\bar{2}\bar{1}$) measured every 97 data. The data were corrected for decay by scaling on the three standards which all decayed similarly (~2%). Corrections for absorption applied empirically on the basis of azimuthal scans of ten reflections spanning a range of 2θ values (minimum and maximum transmission 0·035 and 0·059 respectively). Crystal solution and refinement carried out using the *SHELXTL* collection of crystallographic software (Sheldrick, 1978). Au position determined from a direct-methods program solution; all remaining non-hydrogen atoms located on difference Fourier maps. Phenyl rings refined as idealized polygons (C—C = 1·395 Å, C—C—C = 120°) using H atoms placed in calculated positions with fixed thermal parameters [$U(\mathrm{H}) = 0{\cdot}08$ Å^2]. All non-hydrogen atoms refined anisotropically. Refinement based on F with weights of the form $w^{-1} = [\sigma^2(F) + 0{\cdot}0002(F^2)]$. The value of $g = 0{\cdot}0002$ was refined by fitting $(F_o - F_c)^2$ to $[\sigma^2(F) + gF^2]/k$ (k scale factor) to put weights on an approximately absolute scale. Scattering factors, including terms for anomalous dispersion, taken from *International Tables for X-ray Crystallography* (1974). Convergence to conventional R values of $R = 0{\cdot}0443$ and $wR = 0{\cdot}0398$ obtained using 208 variable parameters and 2703 reflections with $F_o^2 > 3\sigma(F_o^2)$. For final cycle maximum shift/$\sigma = 0{\cdot}01$ with a goodness-of-fit indicator of 1·189. Residual electron density on final difference Fourier map of +1·53 and −0·8 e Å^{-3} in the vicinity of C(2).*

Discussion. The product obtained from the reaction of $\mathrm{AuCl_3}$(pyridine) with $\mathrm{Na}[3,5\text{-}(\mathrm{C_6H_5})_2\mathrm{C_3HN_2}]$ is a trinuclear mixed-valence gold–pyrazolate complex. The unit cell contains four molecules of this complex and no solvent molecules. A perspective view of the complex is shown in Fig. 1. Atomic positional and equivalent

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*The highest peak of residual electron density [1·63 Å from C(2)] could be accounted for by partial chlorination of this position. Halogenation of the 4-position of pyrazolates is a commonly observed feature of this chemistry. As the SOF of this chlorine atom refined to < 0·20, it was not included in the final refinement of the structure.

isotropic thermal parameters for all non-hydrogen atoms are presented in Table 1.* Bond angles and distances are summarized in Table 2.

The structure reported here contains an almost planar nine-membered metallocycle, $[\mathrm{Au{-}N{-}N}]_3$. The carbon atoms of the pyrazolate ligands deviate as much as 0·33 (5) Å from the best-fit plane of the metallocycle while the phenyl groups rotate out of this plane. The overall symmetry of the complex is C_{2v} (assuming free rotation of the phenyl groups).

Two of the gold atoms, Au(2) and Au(3), are two-coordinate linear [178·2 (6), 179·0 (7)°] N-bound $\mathrm{Au^I}$ centers. The third gold atom, Au(1), is four-coordinate square planar (within 1·3°) $\mathrm{Au^{III}}$ with *trans* chloride and pyrazolate ligands. The angles formed between the chloride and pyrazolate ligands bound to Au(1) are 90 (2)°. The Au—Cl bond lengths measured here, 2·274 (7) and 2·284 (7) Å, are typical of *trans* $\mathrm{Au^{III}}$ complexes (Porter, Murray & Fackler, 1987).

It is interesting to compare the structure of $[\mathrm{Au}\text{-}\mu\text{-}\{3,5\text{-}(\mathrm{C_6H_5})_2\mathrm{C_3HN_2}\}]_3\mathrm{Cl_2}$ reported here, containing an $\mathrm{Au^I_2Au^{III}}$ metal core, with the structure of its unoxidized precursor $[\mathrm{Au}\text{-}\mu\text{-}\{3,5\text{-}(\mathrm{C_6H_5})_2\mathrm{C_3HN_2}\}]_3$ (Murray, Raptis & Fackler, 1988) containing an $\mathrm{Au^I_3}$ core. The $\mathrm{Au^{III}}$—N bonds, 1·986 (14) and 2·000 (15) Å, are similar in length to the $\mathrm{Au^I}$—N bonds, 1·984 (16)–2·013 (14) Å, in $\mathrm{Au^I_2Au^{III}}$ and statistically indistinguishable from the Au—N bond length in $\mathrm{Au^I_3}$, 1·978 (9) Å. The geometries of the pyrazolate rings remain unaffected by the oxidation states of the metals of the trinuclear core. The N—N, N—C and C—C bond lengths measured in the $\mathrm{Au^I_2Au^{III}}$ complex described here range between 1·364 (21) and 1·417 (21),

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

	x	y	z	U/U_{eq}
Au(1)	10624 (1)	5972 (1)	2350 (1)	41 (1)*
Au(2)	8856 (1)	5949 (1)	2970 (1)	42 (1)*
Au(3)	10601 (1)	6420 (1)	3656 (1)	44 (1)*
Cl(1)	10491 (4)	8289 (7)	2200 (3)	73 (3)*
Cl(2)	10737 (4)	3647 (7)	2513 (3)	79 (3)*
N(1)	9590 (9)	5695 (18)	1941 (5)	42 (7)*
N(2)	8859 (10)	5696 (18)	2204 (6)	45 (7)*
N(3)	8825 (9)	6247 (18)	3738 (5)	44 (6)*
N(4)	9546 (9)	6592 (18)	4020 (5)	44 (6)*
N(5)	11665 (8)	6210 (17)	3292 (6)	41 (6)*
N(6)	11645 (8)	6243 (18)	2761 (6)	43 (7)*
C(1)	9420 (12)	5633 (20)	1424 (7)	42 (6)
C(2)	8554 (12)	5628 (22)	1333 (8)	53 (6)
C(3)	8262 (13)	5685 (23)	1831 (8)	50 (6)
C(4)	8196 (12)	6302 (24)	4063 (8)	52 (6)
C(5)	8476 (12)	6718 (21)	4567 (8)	50 (6)
C(6)	9327 (11)	6910 (21)	4496 (7)	38 (6)
C(7)	12456 (12)	6143 (22)	3450 (7)	44 (6)
C(8)	12949 (11)	6099 (21)	3011 (7)	43 (5)
C(9)	12418 (12)	6188 (22)	2571 (7)	45 (6)
C(11)	10063 (8)	6501 (14)	619 (6)	69 (7)
C(12)	10664	6469	244	89 (9)
C(13)	11304	5526	292	90 (9)
C(14)	11342	4615	714	82 (9)
C(15)	10741	4647	1089	60 (7)
C(16)	10101	5590	1041	52 (6)
C(31)	7104 (7)	6869 (12)	2261 (5)	41 (6)
C(32)	6277	6950	2365	53 (7)
C(33)	5749	5922	2180	63 (7)
C(34)	6047	4812	1891	55 (7)
C(35)	6873	4730	1788	49 (6)
C(36)	7402	5759	1973	44 (6)
C(41)	6757 (8)	6925 (12)	4033 (5)	54 (7)
C(42)	5956	6650	3879	65 (7)
C(43)	5773	5460	3589	54 (7)
C(44)	6391	4546	3454	71 (8)
C(45)	7192	4822	3608	46 (6)
C(46)	7375	6011	3898	41 (5)
C(61)	10464 (9)	8360 (15)	4833 (4)	63 (7)
C(62)	10986	8788	5236	85 (8)
C(63)	10955	8144	5722	74 (8)
C(64)	10402	7073	5804	86 (9)
C(65)	9880	6645	5401	67 (7)
C(66)	9911	7289	4915	51 (6)
C(71)	12264 (7)	6456 (15)	4425 (6)	75 (8)
C(72)	12582	6391	4932	66 (7)
C(73)	13366	5886	5022	76 (8)
C(74)	13831	5446	4606	83 (9)
C(75)	13513	5511	4099	79 (8)
C(76)	12729	6016	4009	38 (5)
C(91)	13171 (9)	5073 (14)	1865 (6)	74 (8)
C(92)	13477	5101	1363	89 (9)
C(93)	13283	6202	1029	72 (7)
C(94)	12784	7275	1199	90 (9)
C(95)	12479	7246	1701	67 (7)
C(96)	12672	6145	2034	51 (6)

* Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°)

Au(1)—Cl(1)	2·274 (7)	N(2)—C(3)	1·360 (26)
Au(1)—Cl(2)	2·284 (7)	N(3)—C(4)	1·345 (25)
Au(1)—N(1)	2·000 (15)	N(4)—C(6)	1·318 (24)
Au(2)—N(2)	1·984 (16)	N(5)—C(7)	1·359 (23)
Au(2)—N(3)	1·995 (13)	N(6)—C(9)	1·375 (23)
Au(3)—N(4)	1·998 (15)	C(1)—C(2)	1·441 (28)
Au(3)—N(5)	2·013 (14)	C(2)—C(3)	1·375 (29)
Au(1)—N(6)	1·986 (14)	C(4)—C(5)	1·424 (28)
N(1)—N(2)	1·392 (22)	C(5)—C(6)	1·430 (27)
N(3)—N(4)	1·417 (21)	C(7)—C(8)	1·403 (26)
N(5)—N(6)	1·364 (21)	C(8)—C(9)	1·419 (26)
N(1)—C(1)	1·353 (23)		

Cl(1)—Au(1)—Cl(2)	178·8 (2)	N(4)—Au(3)—N(5)	179·0 (7)
Cl(1)—Au(1)—N(1)	87·9 (5)	Au(1)—N(1)—N(2)	118·7 (11)
Cl(1)—Au(1)—N(6)	92·2 (5)	Au(2)—N(2)—N(1)	120·1 (11)
Cl(2)—Au(1)—N(1)	91·8 (5)	Au(2)—N(3)—N(4)	120·1 (10)
Cl(2)—Au(1)—N(6)	88·0 (5)	Au(3)—N(4)—N(3)	117·9 (10)
N(1)—Au(1)—N(6)	179·6 (8)	Au(3)—N(5)—N(6)	117·3 (10)
N(2)—Au(2)—N(3)	178·2 (6)	Au(1)—N(6)—N(5)	122·1 (10)

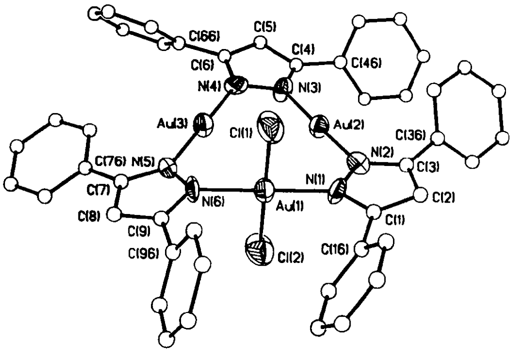

Fig. 1. A perspective view of the $[\mathrm{Au}\text{-}\mu\text{-}\{3,5\text{-}(\mathrm{C_6H_5})_2\mathrm{C_3HN_2}\}]_3\mathrm{Cl_2}$ structure. Thermal ellipsoids have been drawn at the 50% probability level. H atoms have not been included. C atoms of arbitrary radii.

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* Lists of structure factors, anisotropic thermal parameters, additional bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44769 (54 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1·345 (25) and 1·375 (23), and 1·375 (29) and 1·441 (28) Å respectively and compare well with the corresponding bond lengths, 1·38 (2), 1·36 (2) and 1·42 (2) Å, measured in the Au^I_3 trimer. The non-bonding Au···Au distances in $Au^I_2Au^{III}$ range between 3·348 (1) and 3·383 (1) Å and on the average are equal in length to the 3·368 (1) Å distance observed for Au^I_3.

The complex reported here, $Au^I_2Au^{III}$, is the two-electron oxidation product of the previously reported Au^I_3 (Murray, Raptis & Fackler, 1988) complex. The oxidation of one of the three Au atoms from the I to the III state does not alter significantly the geometry of the nine-membered metallocycle or the bridging pyrazolate rings. However, the high symmetry, D_{3h} (ignoring the phenyl groups), observed for the Au^I_3 complex which crystallized in the crystallographic space group $R\bar{3}c$, is reduced to C_{2v} in the $Au^I_2Au^{III}$ complex which crystallizes in the space group $P2_1/c$. The yet unknown analogous complexes $Au^IAu^{III}_2$ and Au^{III}_3 will have C_{2v} and D_{3h} symmetries respectively. Work towards the characterization of these species is under way.

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The Structure of the Tetraphenylarsonium Salt of the Trichloro(pentane-2,4-dionato)nitrosyltechnetium(II) Anion

By D. S. Brown, J. L. Newman and J. R. Thornback

*Department of Chemistry, Loughborough University of Technology, Loughborough, Leics LE*11 3*TU, England*

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Abstract. Tetraphenylarsonium trichloro(pentane-2,4-dionato)nitrosyltechnetate(II), $[As(C_6H_5)_4][Tc(NO)Cl_3(C_5H_7O_2)]$, $M_r = 717·4$, triclinic, $P\bar{1}$, $a = 10·261$ (4), $b = 11·261$ (10), $c = 13·686$ (10) Å, $\alpha = 101·7$ (5), $\beta = 91·9$ (5), $\gamma = 97·3$ (5)°, $U = 1532·93$ Å^3, $Z = 2$, D_m not measured, $D_x = 1·554$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 18·15$ cm^{-1}, $F(000) = 718$, $T = 293$ K, $R = 0·076$ for 2008 observed reflexions with $I > 3\sigma(I)$. The anion $[Tc(NO)Cl_3(C_5H_7O_2)]^-$ has a distorted octahedral geometry with three Cl atoms, a bidentate pentane-2,4-dione ligand and the nitrosyl *trans* to either of the equivalent oxygens. The other *trans* position is occupied by a Cl atom resulting in a disordered structure.

Introduction. The use of technetium-99m ($t_{1/2} = 6·02$ h) in the field of nuclear medicine is well established, while technetium-99 ($t_{1/2} = 2·1 \times 10^5$ a) enables extensive research into the coordination chemistry of the element. We are interested, in particular, in the synthesis of Tc complexes as possible radiopharmaceuticals in which the Tc atom is in a low oxidation state. Stabilization of low oxidation state requires the presence of a π-acid ligand, which in the complexes we have studied is the NO group. Recently we reported the structure of the complex $[TcNOCl_4(CH_3OH)]^-$ (Brown, Newman, Thornback & Davison, 1987) and its synthesis on a no-carrier added (^{99m}Tc) scale (Cheah, Newman, Nowotnik & Thornback, 1987). This complex is an

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