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Syntheses of dinuclear gold(I) ring complexes containing 1,1-dicyanoethene-2,2-dithiolate-*S*,*S* and bis(diphosphines) as bridging ligands. X-ray crystal structure of $[Au_2\mu\text{-(i-MNT)}\mu\text{-(dppee)}]$

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Abstract

The reaction of $[Au_2\mu\text{-bis(diphosphine)}Cl_2]$ with potassium 1,1-dicyanoethene-2,2-dithiolate $[K_2\text{(i-MNT)}]$, yields the heterobridged complexes: $[Au_2\mu\text{-(i-MNT)}\mu\text{-(dppee)}]$ (**1**) (dppee = bis(diphenylphosphinoethylene)), $[Au_2\mu\text{-(i-MNT)}\mu\text{-(dppe)}]$ (**2**) (dppe = bis(diphenylphosphino)ethane), $[Au_2\mu\text{-(i-MNT)}\mu\text{-(dppb)}]$ (**3**) (dppb = bis(diphenylphosphino)butane), $[Au_2\mu\text{-(i-MNT)}\mu\text{-(dppAs)}]$ (**4**) (dppAs = (diphenylarsino)(diphenylphosphino)-ethane). The molecular structure of **1** is described. Complex **1** crystallized in the triclinic space group $P\bar{1}$ with $a = 10.451(2)$, $b = 11.774(1)$, $c = 13.432(2)$ Å, $\alpha = 65.40(1)$, $\beta = 82.30(1)$, $\gamma = 77.75(1)°$ and $V = 1466.6(4)$ Å^3. The structure features two linear two-coordinate gold(I) centers bridged by the i-MNT ligand on one side and by a bis(diphosphine) ligand on the other forming a dinuclear complex with an Au···Au distance of 2.867(1) Å in a twisted nine-membered ring structure.

Key words: Crystal structures; Gold complexes; Dithiolate complexes; Diphosphine complexes; Dinuclear complexes

Introduction

The synthesis of dinuclear metallic complexes provides a handle for the study of metal–metal interactions. Particular attention in our group has been given to the synthesis and characterization of dinuclear gold(I) systems [1–4]. Dinuclear gold(I) complexes have provided structural and spectroscopic evidence for the attractive interaction observed between gold atoms [5] which has been attributed to relativistic effects [6].

We reported previously [7] the synthesis and structural characterization of $[n\text{-}Bu_4N]_2[Au_2\text{(i-MNT)}_2]$. The molecular structure of this complex showed an eight-membered ring with two i-MNT units bridging the two gold(I) centers. The metal–metal distance was found to be 2.78 Å. Yet Au···Au interactions are generally much longer in complexes not having bridging ligands but containing S–Au–S coordination [8]. With phosphine complexes of the type L–Au–X, L = phosphine, Li and Pyykkö [9] recently suggested that the strongest interactions should be observed when X is a very soft ligand. The Au···Au distance in $Au_2(Et_2PCH_2CH_2S)_2$, however, is considerably longer (3.156(1) Å) than the distances observed in $[Au_2\text{(i-MNT)}_2]^{2-}$ or other eight-membered ring complexes with linear S–Au–S coordination. Added interest in P–Au–S coordination comes from the use of gold drugs with this type of geometry, such as Auranofin [10], to treat rheumatoid arthritis.

In our study of dinuclear gold(I) complexes with metal–metal interactions we have engaged in the synthesis of hetero-bridged ring systems of the type $[Au_2\mu\text{-(i-MNT)}\mu\text{-bis(diphosphine)}]$. In these complexes, linear S–Au–P coordination occurs at both gold(I) centers: the use of bis(diphosphine) ligands allows an increase of the ring nuclearity through incorporation of methylene units between the phosphorus centers. In the 'open ring' or 'horseshoe' complex $[Au_2\mu\text{-(i-MNT)}(PPh_3)_2]$ the Au···Au distance is 3.156 Å, about the

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same as in the ten-membered ring of $Au_2(Et_2PCH_2CH_2S)_2$.

Here we report the synthesis and structural characterization of the hetero-bridged complex [$Au_2\mu$-(i-MNT)μ-(dppee)]. The syntheses of analogous complexes containing dppe, dppb and dppAs as bridging ligands are also described.

Experimental

All reactions were carried out in oven-dried Schlenk glassware by using standard inert atmosphere techniques. Dry and freshly distilled solvents were used for all reactions. The bis(diphosphine) ligands were purchased from Strem Chemical Corp. K_2(i-MNT) was synthesized according to literature procedures [11]. $Au_2(\mu$-dppee)$(Cl)_2$, $Au_2(\mu$-dppe)$(Cl)_2$, $Au_2(\mu$-dppb)$(Cl)_2$ and $Au_2(\mu$-dppAs)$(Cl)_2$ were synthesized by displacement of THT (tetrahydrothiophene) from 2 equiv. of Au(THT)Cl with the corresponding bis(diphosphine) ligand.

^1H and $^{31}P\{^1H\}$ NMR spectra were obtained using $CDCl_3$ as solvent and were recorded at room temperature on a Varian XL-200 MHz Fourier Transform spectrometer. For ^1H NMR, $SiMe_4$ was used as the internal standard. The $^{31}P\{^1H\}$ NMR spectra were referenced against external H_3PO_4. IR spectra were recorded as Nujol mulls or KBr pellets on a Perkin-Elmer 783 spectrophotometer. Microanalyses were performed by Galbraith Laboratories Inc.

Syntheses

$Au_2\mu$-(i-MNT)μ-(dppee) (1)

To an MeOH (5 ml) solution of K_2(i-MNT) (0.0193 g, 0.0887 mmol), $Au_2(\mu$-dppee)$(Cl)_2$ (0.0694 g, 0.0806 mmol) was added. A yellow suspension formed. The reaction was allowed to stir for 3 h. The MeOH was evaporated under vacuum and CH_2Cl_2 (5 ml) was added to the yellow solid obtained. The yellow CH_2Cl_2 solution was filtered and concentrated under vacuum. Et_2O (10 ml) was added to precipitate the product as a bright yellow solid. The solid was filtered, washed with Et_2O and dried under vacuum. Yield 0.0604 g (80.5%). IR: 2200 (s, C≡N) 1580, 1570 (w, C=C, Ph) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 19.02$ ppm. *Anal.* Calc.: C, 38.72; H, 2.38; N, 3.01. Found. C, 38.48; H, 2.62; N, 2.53%.

The same general procedure was followed for complexes **2**–**4**. Specific experimental details and characterization data are as follows.

$Au_2\mu$-(i-MNT)μ-(dppe) (2)

To a CH_2Cl_2 (5 ml) solution of Au_2(dppe)$(Cl)_2$ (0.185 g, 0.215 mmol), K_2(i-MNT) was added. The reaction was stirred for 3 h. A light brown solid was obtained. Yield 0.148 g (74%). IR: 2190 (s, C≡N) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 30.74$(s) ppm. *Anal.* Calc.: C, 38.64; H, 2.59; N, 3.00. Found: C, 37.88; H, 2.65; N, 2.54%.

$Au_2\mu$-(i-MNT)μ-(dppb) (3)

To a CH_2Cl_2 solution containing Au_2(dppb)$(Cl)_2$ (0.0927 g, 0.104 mmol), K_2(i-MNT) (0.0227 g, 0.104 mmol) was added. The reaction was stirred for 3.5 h. The product was obtained as a light yellow solid. Yield 0.0840 g (87.4%). IR: 2210 (s, C≡N), 1585, 1570 (w, C=C, Ph) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 31.97$ ppm. ^1H ($CDCl_3$): $\delta = 1.86$ (m, CH_2–CH_2–CH_2–CH_2 broad), 2.7 (m, CH_2–CH_2–CH_2–CH_2 broad) ppm. *Anal.* Calc.: C, 40.01; H, 2.94; N, 2.92. Found: C, 38.25; H, 2.81; N, 2.49%.

$Au_2\mu$-(i-MNT)μ-(dppAs) (4)

To a MeOH (5 ml) solution of K_2(i-MNT), $Au_2(\mu$-dppAs)$(Cl)_2$ (0.0928 g, 0.102 mmol) was added. Acetone (10 ml) was added to the resulting suspension. After 2 h the solvent mixture was evaporated through vacuum. The yellow solid obtained was washed with MeOH and filtered. Yield 0.0662 g (68%). IR: 2200 (s, C≡N) cm^{-1}. *Anal.* Calc.: C, 36.90; H, 2.48; N, 2.87. Found: C, 36.87; H, 2.48; N, 2.58%.

X-ray data collection and reduction

Yellow crystals of **1** suitable for X-ray crystallography were grown from the slow diffusion of Et_2O into a CH_2Cl_2 solution. A crystal with dimensions 0.20 × 0.20 × 0.20 mm was mounted on a glass fiber with epoxy cement in a random orientation. The unit cell was determined from 25 machine centered reflections, $15 \leq 2\theta \leq 24°$. Data were collected on a Nicolet R3m/E diffractometer controlled by a Data General NOVA 4 minicomputer using Mo Kα radiation at ambient

TABLE 1. Crystallographic data for $Au_2\mu$-(i-MNT)μ-(dppee)

Formula	$Au_2S_2P_2N_2C_{30}H_{22}$
Formula weight	930.5
a (Å)	10.451(2)
b (Å)	11.774(1)
c (Å)	13.432(2)
α (°)	65.40(1)
β (°)	82.30(1)
γ (°)	77.75(1)
V (Å^3)	1466.6(4)
Z	2
D_{calc} (g/cm^{-3})	2.107
μ(Mo Kα) (cm^{-1})	102.42
λ(radiation)[a] (Å)	0.71073
Temperature (°C)	23
Transmission factor: max., min.	0.955, 0.713
R[b], R_w[c]	0.0483, 0.0562

[a] Graphite-monochromated Mo Kα. [b] $R = \Sigma||F_o| - |F_c||/\Sigma F_o$. [c] $R_w = \{[\Sigma w(F_o - F_c)^2]/[\Sigma w(F_o)^2]\}^{1/2}$; $w^{-1} = [\sigma^2 F + gF^2]$

temperature for $4 \leqslant 2\theta \leqslant 45°$. A total of 4082 reflections was measured of which 2687 were considered unique and observed. Three standard reflections were measured every 97 reflections. No significant intensity variations were observed. The data were corrected for absorption, Lorentz and polarization effects. Solution and refinement were performed using SHELXTL [12] crystallographic computational package on a Micro VAX II.

Triclinic symmetry was suggested by interaxial angles and confirmed by axial photographs and Delaunnay reduction. The space group $P\bar{1}$ was confirmed by successful structure refinement. Initial gold atoms positions were obtained from the direct methods program solution. The remaining atoms were located by cycles of least-squares refinement based on F and difference Fourier maps. Hydrogen atoms were placed in idealized positions (C–H = 0.96 Å) and with thermal parameters fixed (U(H) = 0.08 Å). All non-hydrogen atoms except phenyl C atoms were refined anisotropically. The final refinement yielded $R = 0.0483$ and $R_w = 0.0562$. Crystal data and collection parameters are found in Table 1. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 2. Relevant bond distances and angles are presented in Table 3.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for [$Au_2\mu$-(i-MNT)μ-(dppee)] (**1**) with e.s.d s in parentheses

	x	y	z	U_{eq}[a]
Au(1)	1584(1)	1159(1)	4789(1)	37(1)
Au(2)	3493(1)	−968(1)	4746(1)	37(1)
S(1)	999(5)	−152(5)	6545(4)	49(2)
S(2)	3910(4)	−1363(5)	6517(4)	48(2)
P(1)	2045(4)	2599(4)	3092(3)	32(2)
P(2)	3137(4)	−766(4)	3046(3)	31(2)
N(1)	4313(21)	−3032(21)	9467(16)	93(12)
N(2)	236(18)	−1398(19)	9480(16)	78(11)
C(1)	2405(16)	−1089(17)	7179(15)	38(8)
C(2)	2311(19)	−1635(17)	8317(15)	45(9)
C(3)	3462(21)	−2456(19)	8943(15)	49(9)
C(4)	1134(23)	−1473(19)	8926(15)	54(10)
C(5)	2898(17)	1926(16)	2146(14)	39(8)
C(6)	2349(15)	800(16)	2132(13)	36(8)
C(10)	3101(16)	3612(16)	3138(13)	34(4)
C(11)	3710(18)	4418(18)	2211(16)	53(5)
C(12)	4488(19)	5204(19)	2260(16)	55(5)
C(13)	4703(20)	5181(20)	3258(17)	61(6)
C(14)	4149(20)	4395(20)	4191(18)	64(6)
C(15)	3313(22)	3613(22)	4136(19)	71(6)
C(20)	585(17)	3611(16)	2443(14)	38(4)
C(21)	−612(19)	3320(19)	2938(16)	53(5)
C(22)	−1754(23)	4093(21)	2465(18)	72(6)
C(23)	−1748(22)	5152(21)	1527(18)	69(6)
C(24)	−539(21)	5483(22)	1033(19)	68(6)
C(25)	603(21)	4708(19)	1500(16)	57(5)
C(30)	4651(16)	−1113(15)	2297(13)	33(4)
C(31)	5820(20)	−1193(19)	2716(17)	59(6)
C(32)	6982(23)	−1366(21)	2102(18)	73(7)
C(33)	6981(20)	−1603(18)	1182(16)	56(5)
C(34)	5837(18)	−1603(18)	843(16)	52(5)
C(35)	4655(19)	−1365(17)	1386(15)	49(5)
C(40)	2041(16)	−1812(16)	3079(13)	36(4)
C(41)	1455(18)	−1648(18)	2158(16)	49(5)
C(42)	667(18)	−2512(18)	2270(16)	51(5)
C(43)	435(21)	−3451(20)	3244(17)	63(6)
C(44)	992(21)	−3615(22)	4168(19)	72(6)
C(45)	1815(17)	−2761(17)	4085(15)	45(5)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Relevant bond lengths (Å) and angles (°) for [$Au_2\mu$-(i-MNT)μ-(dppee)] (**1**) with e.s.d.s in parentheses

Bond lengths			
Au(1)–Au(2)	2.867(1)	P(1)–C(5)	1.81(2)
Au(1)–S(1)	2.303(4)	P(2)–C(6)	1.82(1)
Au(1)–P(1)	2.266(4)	N(1)–C(3)	1.12(3)
Au(2)–S(2)	2.310(5)	N(2)–C(4)	1.13(3)
Au(2)–P(2)	2.269(5)	C(1)–C(2)	1.39(2)
S(1)–C(1)	1.72(2)	C(2)–C(3)	1.48(3)
S(2)–C(1)	1.74(2)	C(2)–C(4)	1.41(3)
		C(5)–C(6)	1.56(3)
Bond angles			
Au(2)–Au(1)–S(1)	86.6(1)	Au(2)–P(2)–C(6)	115.8(7)
Au(2)–Au(1)–P(1)	98.6(1)	S(1)–C(1)–S(2)	126.(1)
S(1)–Au(1)–P(1)	174.7(2)	S(1)–C(1)–C(2)	116.(1)
Au(1)–Au(2)–S(2)	86.8(1)	S(2)–C(1)–C(2)	118 (1)
Au(1)–Au(2)–P(2)	97.6(1)	C(1)–C(2)–C(3)	120.(2)
S(2)–Au(2)–P(2)	175.0(2)	C(1)–C(2)–C(4)	123.(2)
Au(1)–S(1)–C(1)	108.2(6)	C(3)–C(2)–C(4)	117.(2)
Au(2)–S(2)–C(1)	106.9(7)	P(1)–C(5)–C(6)	115.(1)
Au(1)–P(1)–C(5)	114.8(5)	P(2)–C(6)–C(5)	115.(1)

Results and discussion

The general reaction for the syntheses of the dinuclear gold(I) rings **1**–**4** involves the reaction of K_2(i-MNT) with the corresponding $Au_2[R_2P(CH_x)_nPR_2](Cl)_2$ (where R = phenyl for $x = 2$, $n = 2$, 4; R = phenyl for $x = 1$, $n = 2$) or with $Au_2[Ph_2As(CH_2)_2PPh_2](Cl)_2$ to form complex **4**. All products are obtained as yellow solids in moderately high yields (67–87%). The typical characterization features include a strong band in the IR around 2200 cm^{-1} corresponding to the C≡N stretch of the i-MNT ligand. Also, a singlet is observed in all cases in the $^{31}P\{^1H\}$ NMR spectra. The appearance of a singlet indicated the presence of two equivalent phosphorus atoms at room temperature, and the observed downfield shift of the singlet relative to that observed in the $^{31}P\{^1H\}$ of the original $Au_2[R_2P(CH_2)_nPR_2](Cl)_2$ complex indicated coordination to the sulfur ligand.

Figure 1 shows the molecular structure of complex **1**. The two gold atoms in complex **1** are bridged on one side by the dppee ligand (Au(1)–P(1) = 2.266(4),

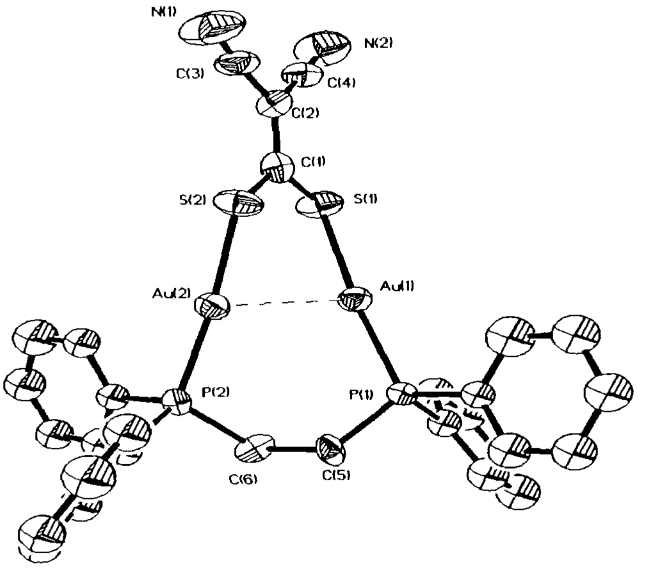

Fig. 1 Molecular structure of [Au$_2\mu$-(i-MNT)μ-(dppee)] with thermal ellipsoids drawn at 50% probability. The Au···Au distance is 2.867(1) Å.

Au(2)–P(2) = 2.269(5) Å), and on the other side by one i-MNT ligand through the sulfur atoms (Au(1)–S(1) = 2.303(4), Au(2)–S(2) = 2.310(5) Å). The coordination around the gold atoms is almost linear: S(1)–Au(1)–P(1) = 174.7(2)° and S(2)–Au(2)–P(2) = 175.0(2)°. The Au(1)···Au(2) distance of 2.867(1) Å indicates significant metal–metal interaction.

The important features to observe in this structure are the expansion of the typical eight-membered dinuclear ring to a nine-membered ring and the close Au···Au contacts present in the structure. The Au(1)–Au(2) distance of 2.867 Å observed in complex **1** is short when compared to that observed in metallic gold (2.884 Å) [13]. This same shortening of the Au···Au distance has been reported for other i-MNT complexes including [n-Bu$_4$N][Au$_2$(i-MNT)$_2$] (2.796(1) Å) [7]. The latter is a homo-bridged planar eight-membered ring.

It is also interesting to compare this structure to that previously reported for [Au$_2$(μ-S(CH$_2$)$_3$-S)(μ-dppm)] [14]. This ten-membered ring contains the saturated propane dithiolate as the bridging sulfur-donor ligand. In this case the longer bite distance of the dithiolate (4.122(4) Å) compared to that of i-MNT (3.076 Å) appears to elongate the Au···Au distance to 3.128(1) Å, while i-MNT causes the metal atoms to be in closer proximity.

Preliminary structural data have also been obtained for [Au$_2\mu$-(i-MNT)μ-(dppAs)] (**4**). It has been difficult to obtain a satisfactory disordered model of the phosphine arsine ligand. Nevertheless, the structure shows short gold–gold contacts of approximately 2.90 Å. This preliminary structure shows a slight twisting of the methylene chain to allow gold–gold interaction. This twisting in the phosphine arsine ligand causes a small deviation from linearity of the S–Au–P chains, but overall the geometry remains the same.

No structural data could be obtained for [Au$_2$(i-MNT)μ-(dppe)] or [Au$_2$(i-MNT)μ-(dppb)]. Several attempts to grow crystals of these complexes were unsuccessful. Nevertheless, the spectroscopic data from these complexes seem to indicate that the structural features to be expected should be very similar to those shown by complex **1**. Even with the eleven-membered ring that would be expected for the dppb complex **3**, we believe that the structure would compromise the small bite distance of the i-MNT ligand with the Au···Au interaction through twisting of the methylene chain of the diphosphine ligand.

Conclusions

Work with the 1,1-dithiolene i-MNT ligand has produced new ring complexes where the nuclearity of the typical eight-membered ring has been increased through the incorporation of methylene units in the bis(diphosphine) ligands. The structural data obtained indicate that Au···Au contacts are maintained even after expansion of the rings. The structures compromise the expansion of the ring and the Au···Au interactions through twisting of the methylene units in the bis(diphosphine) ligands and small deviations from linearity in the S–Au–P chains.

Supplementary material

Tables of anisotropic displacement parameters, hydrogen coordinates, and observed and calculated structure factors are available from the authors upon request.

Acknowledgements

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