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Influence of anions and crystallisation conditions on the solid-state structure of some binuclear silver(I) complexes supported by triazolopyrimidine bridges

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The reaction of silver salts AgX (X = NO_3 or $\frac{1}{2}SO_4$) with [1,2,4]triazolo[1,5-*a*]pyrimidine (tp) in aqueous media afforded the silver(I) binuclear complexes $[Ag_2(NO_3)_2(\mu\text{-tp-}N^3,N^4)_2]$ **1**, $[Ag_2(SO_4)(\mu\text{-tp-}N^3,N^4)_2(H_2O)]\cdot H_2O$ **2**, $[Ag_2(SO_4)(\mu\text{-tp-}N^3,N^4)_3(H_2O)]\cdot 3H_2O$ **3** and $[Ag_2(SO_4)_2(Htp)_2]$ **4**. The compounds have been structurally characterised by spectroscopic methods (IR, ^{1}H, ^{13}C NMR) and X-ray crystallography (**1**, **2** and **3**). The X-ray results show that the complexes comprise dimeric units in which the silver atoms are bridged by two (**1**, **2**) or three (**3**) tp ligands, giving rise to intermetallic contacts of 3.117(1), 3.127(1) and 3.089(1) Å respectively for **1**, **2** and **3**. The crystallisation conditions and/or the nature of the anion appear to play an important role in the stereochemistry of the silver centres. The NMR studies in D_2O suggest that the ligand exhibits in solution the same co-ordination mode as found in the solid state.

Relativistic effects appear to be related to the pronounced tendency of heavy metal ions with d^{10} configuration to exhibit linear co-ordination. The stabilisation of the 5s orbital as a consequence of relativistic effects favours the formation of efficient s/d or s/p hybridisations which are responsible for the formation of linear two-co-ordinated complexes, gold(I) being the most representative example.[1] In the case of silver(I) relativistic effects are less pronounced than with gold(I) and therefore a greater variety of co-ordination modes is adopted. Many factors, such as the nature of the ligands, solvent, steric requirements of anions, *etc*., appear to modulate the stereochemistry of silver complexes. The plasticity of silver(I) is conveniently illustrated with the pyrazine (pyz) system. Thus, co-ordination modes range from linear as found in the one-dimensional polymer $\{[Ag(pyz)]BF_4\}_n$[2] to octahedral in the cubic framework of $\{[Ag(pyz)_3]SbF_6\}_n$.[3] Our previous studies on the co-ordination of silver(I) to substituted triazolopyrimidine derivatives have shown the versatility of such systems, which lead to the formation of either binuclear[4] or polymeric metal complexes[5] depending on the nature of the ligand, anions, reaction conditions and presence of additional ligands.

As a continuation of these studies we now report the interaction of the silver salts $AgNO_3$ and Ag_2SO_4 with unsubstituted [1,2,4]triazolo[1,5-*a*]pyrimidine (tp) in aqueous media, which yields binuclear complexes supported by two or three tp-N^3,N^4 bridges. Although this compound has the ability to bridge metal ions through the N^1, N^3 donor positions in complexes of first-row divalent transition metals,[6] there are no previous reports of a bidentate action through the two adjacent N^3, N^4 positions, which may eventually lead to direct metal–metal interactions.

Experimental

Reactants and methods

[1,2,4]Triazolo[1,5-*a*]pyrimidine (tp) from Aldrich Chemical Co. was used as received. The other chemical reagents and solvents were supplied by commercial sources. All experiments were performed in air.

Preparations

$[Ag_2(NO_3)_2(\mu\text{-tp-}N^3,N^4)_2]$ 1. An aqueous solution of tp (2 mmol in *ca*. 10 cm^3 water) was mixed with $AgNO_3$ (2 mmol) in water (*ca*. 10 cm^3). From the resulting solution, in the following days, pale yellow crystals of complex **1** were recovered. Yield 80% [Found (Calc. for $C_5H_4AgN_5O_3$: C, 20.8 (20.7); H, 1.4 (1.4); N, 24.4 (24.2)%]. IR data (selected bands, cm^{-1}): 580w, 655s, 715w, 780s, 825s, 940w, 1035w, 1180s, 1260s, 1310vs, 1380vs, 1515s, 1540s, 1620s and 3060s. ^{1}H NMR (D_2O): δ 7.75 [dd, H^6, $J(H^6H^7)$ 6.8, $J(H^6H^5)$ 4.8], 8.85 (s, H^2), 9.21 [d, H^5, $J(H^5H^6)$ 4.8, $J(H^5H^7)$ 1.7] and 9.49 [d, H^7, $J(H^7H^6)$ 6.8, $J(H^7H^5)$ 1.7 Hz]. ^{13}C NMR (D_2O): δ 160.9 (s, C^2), 156.3 (s, C^5), 154.8 (s, C^{3A}), 141.7 (s, C^7) and 114.5 (s, C^6).

$[Ag_2(SO_4)(\mu\text{-tp-}N^3,N^4)_2(H_2O)]\cdot H_2O$ 2. This complex was prepared using a similar procedure to that described for **1** but using Ag_2SO_4 instead of $AgNO_3$. After 1 week at room temperature a small amount of pale yellow crystals of **2** was recovered. Yield 16% [Found (Calc. for $C_{10}H_{12}Ag_2N_8O_6S$: C, 20.6 (20.4); H, 2.1 (2.1); Ag, 37.5 (36.7); N, 19.6 (19.1); S, 5.5 (5.4)%]. IR data (selected bands, cm^{-1}): 600w, 615s, 780s, 800s, 980w, 1110vs, 1260s, 1310s, 1390s, 1515s, 1530s, 1620s, 3085s and 3450s. ^{1}H NMR (D_2O): δ 7.73 [dd, H^6, $J(H^6H^7)$ 6.8, $J(H^6H^5)$ 4.8], 8.89 (s, H^2, 9.27 [d, H^5, $J(H^5H^6)$ 4.8, $J(H^5H^7)$ 1.7] and 9.50 [d, H^7, $J(H^7H^6)$ 6.8, $J(H^7H^5)$ 1.7 Hz]. ^{13}C NMR (D_2O): δ 161.2 (s, C^2), 156.4 (s, C^5), 154.6 (s, C^{3A}), 141.7 (s, C^7) and 114.6 (s, C^6).

$[Ag_2(SO_4)(\mu\text{-tp-}N^3,N^4)_3(H_2O)]\cdot 3H_2O$ 3. This complex was prepared using the procedure described above for **2**, but allowing the solution to stand at 4 °C for 24 h. Large tabular yellow crystals of **3** were obtained. Yield 53% [Found (Calc. for $C_{15}H_{20}Ag_2N_{12}O_8S$: C, 23.5 (24.0); H, 2.9 (2.7); Ag, 28.7 (29.0); N, 22.3 (22.6); S, 4.3 (4.3)%]. IR data (selected bands, cm^{-1}): 600w, 620s, 780vs, 800s, 925w, 1120vs, 1190vs, 1260vs, 1310vs, 1395s, 1515vs, 1535vs, 1620vs, 3085s and 3450s. ^{1}H NMR (D_2O): δ 7.65 [dd, H^6, $J(H^6H^7)$ 6.8, $J(H^6H^5)$ 4.7], 8.77 (s, H^2),

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9.15 [d, H^5, $J(H^5H^6)$ 4.7, $J(H^5H^7)$ 1.7] and 9.38 [d, H^7, $J(H^7H^6)$ 6.8, $J(H^7H^5)$ 1.7 Hz]. ^{13}C NMR (D_2O): δ 160.3 (s, C^2), 156.4 (s, C^5), 154.9 (s, C^{3A}), 141.0 (s, C^7) and 114.3 (s, C^6).

$[Ag_2(SO_4)_2(Htp)_2]$ 4. The addition of concentrated H_2SO_4 (0.2 cm^3) to a solution containing Ag_2SO_4 (2 mmol) and tp (2 mmol) in water (*ca.* 20 cm^3) resulted in immediate precipitation of complex **4**. Yield 92% [Found (Calc. for $C_5H_5AgN_4O_4S$: C, 18.6 (18.5); H, 1.5 (1.5); N, 17.2 (17.2); S, 10.1 (9.9)%]. IR data (selected bands, cm^{-1}): 620s, 780vs, 800s, 925w, 1115vs, 1250m, 1310m, 1350m, 1400m, 1545s, 1620m, 1640s, 2905m, 3020m, 3050m and 3450s.

Instrumentation

Microanalyses of C, H, N and S were performed with a Fisons-Instruments EA-1008 analyser at the Instrumentation Centre of the University of Granada, whereas Ag was determined thermogravimetrically by means of Mettler TA-3000 equipment provided with a Mettler TG-50 thermobalance and a heating rate of 20 K min^{-1}, using an atmosphere of pure air (100 cm^3 min^{-1}). Infrared spectra were recorded in the 4000–180 cm^{-1} range on a Perkin-Elmer 983G spectrophotometer, using KBr and polyethylene pellets, NMR spectra in D_2O on a Bruker AM-300 FT spectrometer using acetone as internal standard at the Instrumentation Centre of the University of Granada. The ^{13}C NMR assignments were made according to Kleinpeter *et al.*[7]

Crystallography

Crystallographic data and details of refinement for compounds **1**–**3** are presented in Table 1. The crystals were mounted on a Nonius CAD-4 diffractometer. The intensity data were corrected for Lorentz-polarization effects and empirically (ψ scans) for absorption. The structures were solved by heavy-atom and Fourier methods applying the SDP package.[8] Full-matrix least-squares refinements were performed with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms of the organic ligands were introduced in idealised positions and were not refined. Those of the water molecules were not considered. In the case of **3** the poor quality of the flat crystals did not allow refinement of the oxygen atoms with anisotropic thermal parameters, and the hydrogen atoms were not introduced in the refinement. So, the agreement parameters are obviously higher than those for **1** and **2**.

CCDC reference number 186/869.

See http://www.rsc.org/suppdata/dt/1998/901/ for crystallographic files in .cif format.

Results and Discussion

The reaction of AgX and tp, in 1 : 1 molar ratio in an aqueous medium, yields silver(I) binuclear complexes of general formula $[Ag_2(\mu\text{-tp-}N^3,N^4)_n]X_2\cdot mH_2O$ ($n = 2$ or 3, X = NO_3 or $\frac{1}{2}SO_4$) in which the tp ligands bridge two silver atoms in a bidentate N^3, N^4 bridging fashion, giving rise to short Ag···Ag contacts. Attempts to prepare complexes with different stoichiometry were also made. However, it appears that the formation of the N^3, N^4 chelate is strongly favoured and so the reaction does not depend on the stoichiometry of the reactants.

Structures of complexes 1 and 2

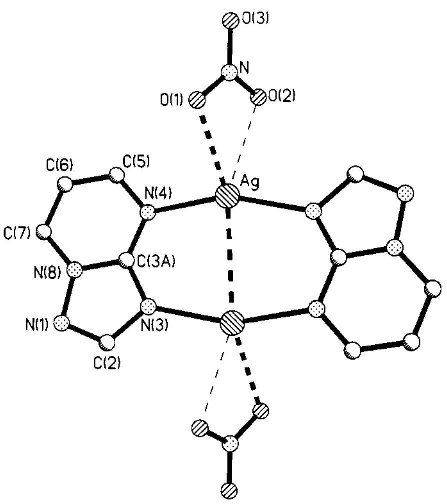

Fig. 1 View of the molecular structure of complex **1**

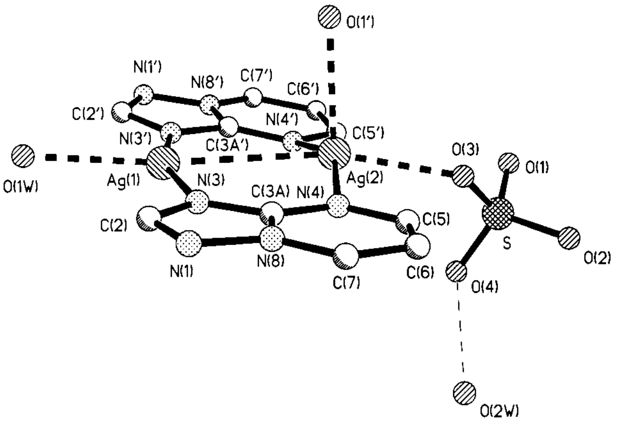

Fig. 2 View of the molecular structure of complex **2**. For clarity the sulfate atom O(1) (1 − *x*, −*y*, 1 − *z*) is also shown

The molecular structures of complexes **1** and **2** are shown in Figs. 1 and 2, respectively and selected interatomic parameters are collected in Table 2. The structures consist of dimeric $Ag_2(\mu\text{-tp-}N^3,N^4)_2$ entities in which two Ag atoms are bridged by two tp ligands and weakly co-ordinated by anions. In **2** co-ordinated and lattice water molecules are also present. The co-ordination geometry about the Ag atoms is distorted linear with additional interactions with the weakly co-ordinated O-donor groups from the anions, water molecules and the second metal centre. The additional Ag–O and Ag···Ag interactions make the effective co-ordination polyhedra 2 + 3 for Ag(1) in **1** and 2 + 2 and 2 + 3 for Ag(1) and Ag(2) respectively in **2** (see Table 2). The co-ordination of the Ag atoms to the tp ligands generates eight-membered $Ag_2N_4C_2$ rings analogous to others reported for ligands with N–C–N motifs.[4,5,9–11] The Ag···Ag separation in both compounds is ≈0.3 Å shorter than the van der Waals radii sum[12] and ≈0.8 Å larger than the N···N distance (2.40 Å) in the N–C–N bite. The latter result may be attributed to the ligand architecture and not to a repulsive Ag···Ag interaction since the N(3) and N(4) donor orbitals are not parallel. The question of a metallophilicity of Cu^I and Ag^I similar to the case of the isoelectronic gold(I) is still a matter of controversy.[4a] However, there are now some scarce examples of ligand-unsupported Ag^I–Ag^I[13,14] and Cu^I–Cu^I[14,15] interactions.

An interesting difference between the two complexes is the relative orientation of the tp ligands (head-to-tail in **1** and head-to-head in **2**), which may be attributed to the different electronic nature and/or steric requirements of the SO_4^{2-} and NO_3^- groups. In the case of **2** also interesting is the pronounced displacement of one of the metal atoms of the dimer [Ag(2)] out of the plane defined by the two tp ligands (0.30 Å). Such displacement appears to facilitate the correct hybridisation of the metal orbitals for the co-ordination of the sulfate donor group O(1) (−*x* + 1, −*y*, −*z* + 1), placed above the $Ag_2(tp)_2$ plane, and linking two dimers related by a crystallographic inversion centre (see Figs. 2 and 3).

Table 1 Crystallographic data and details of refinement for compounds **1**–**3***

	1	**2**	**3**
Formula	$C_{10}H_8Ag_2H_{10}N_{10}O_6$	$C_{10}H_{12}Ag_2N_8O_6S$	$C_{15}H_{20}Ag_2N_{12}O_8S$
M	580.0	588.0	744.2
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbcm*
a/Å	5.778(1)	8.556(3)	11.165(3)
b/Å	7.679(1)	9.728(1)	17.917(2)
c/Å	9.759(2)	10.345(2)	12.873(2)
α/°	67.36(1)	87.18(1)	—
β/°	84.84(2)	75.23(2)	—
γ/°	79.78(1)	76.33(2)	—
U/Å^3	393.2	808.9(3)	2575(1)
Z	1	2	4
Crystal dimensions/mm	0.5 × 0.5 × 0.5	0.025 × 0.30 × 0.40	0.05 × 0.25 × 0.25
D_c/g cm^{-3}	2.451	2.415	1.920
F(000)	280	572	1408
μ(Mo-Kα)/mm^{-1}	2.5	2.5	1.6
h, k, l Ranges	0–7, −9 to 10, −13 to 13	−12 to 12, −13 to 13, 0–14	0–15, 0–25, 0–18
Maximum, minimum transmission	99.9, 77.0	99.9, 66.6	99.9, 88.3
Maximum feature in ΔF map/e Å^{-3}	0.7	0.7	2
No. parameters refined	128	269	175
No. independent reflections	2280	4188	3892
No. observed reflections [$I>3\sigma(I)$]	1990	2731	2584
R	0.023	0.053	0.079
R'	0.037	0.065	0.132
Weighting scheme	$4F_o^2/[\sigma^2(F_o^2) + (0.06F_o^2)^2]$	$4F_o^2/[\sigma^2(F_o^2) + (0.07F_o^2)^2]$	$4F_o^2/[\sigma^2(F_o^2) + (0.10F_o^2)^2]$
Goodness of fit	1.10	1.55	2.4

* Details in common: 291 K; λ(Mo-Kα) 0.710 73 Å; 2θ range 2–60°; $R = ||F_o| - |F_c|/\Sigma|F_o|$; $R' = \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}}$.

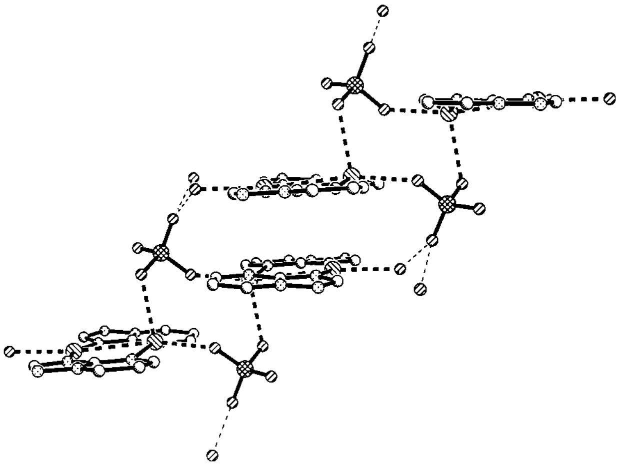

Fig. 3 Perspective view of the packing of complex **2** along the crystallographic b axis

Structure of complex 3

The structure of complex **3** is also built up of binuclear molecules supported by N^3, N^4 triazolopyrimidine bridges but, in this case, three bridging ligands are present (Fig. 4). The molecule presents C_s symmetry as a result of the presence of a crystallographic mirror plane which contains the metal centres, one of the ligands, the sulfur and two oxygen atoms of the anion. The places defined by this ligand and each of the other two is tilted by 105.1(1)° whereas the two crystallographically equivalent ligands form a dihedral angle of 142.6(1)°. Both Ag atoms show distorted trigonal-bipyramidal environments. In the co-ordination polyhedron of Ag(1) the equatorial positions are occupied by three strongly co-ordinated N donor atoms from the tp ligands, whereas a weakly bonded water molecule and the second metal centre lie at the apical positions. For Ag(2), the environment is similar except for a strongly co-ordinated sulfate group (Table 2) instead of the water molecule. Atoms Ag(1) and Ag(2) are displaced 0.305(1) and 0.397(1) Å respectively from the plane defined by the N-donor atoms making the intermetallic distance ≈0.7 Å larger than the N · · · N distance in the N–C–N bite. The presence of three bridges in this case appears to be responsible for a shortening in the Ag · · · Ag intermetallic distance of nearly 0.04 Å compared to those of the previously mentioned doubly bridged compounds.

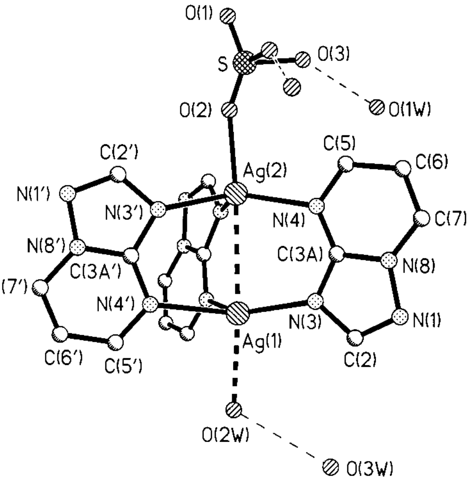

Fig. 4 View of the molecular structure of complex **3**. There is a crystallographic mirror plane containing Ag(1), Ag(2), the ligand N(1), N(3), N(4), N(8), C(2), C(3A), C(5), C(6), C(7), S, O(1), O(2), O(2W) and O(3W) atoms

Infrared spectroscopy

Infrared spectra of tp and complexes **1**, **2** and **3** are virtually identical above 300 cm^{-1}, differing only by the presence of absorption bands due to the presence of NO_3 and SO_4 entities in the complexes. In the case of **4** the tp bands appear considerably shifted to higher frequencies (≈20 cm^{-1}). This observation may be indicative that protonation takes place in the tp moieties rather than in the SO_4^{2-} groups, in contrast to analogous silver complexes containing the methylated derivative 5,7-dimethyl-[1,2,4]triazolo[1,5-*a*]pyrimidine.[4b] A feasible explanation for the different behaviour of the unsubstituted compound may be related to steric reasons. Thus, for the unsubstituted compound,

Table 2 Selected interatomic parameters [distances in Å and angles in (°)] for compounds **1**–**3**

Compound **1**

Ag···Ag^{i}	3.117(1)	Ag–N(3^{i})	2.165(2)
Ag–N(4)	2.220(2)	Ag–O(1)	2.525(2)
Ag–O(2)	2.696(2)		
N(3^{i})–Ag–N(4)	156.8(1)		

Symmetry relation: i $-x, -y, -z$.

Compound **2**

Ag(1)···Ag(2)	3.1266(6)	Ag(1)–N(3)	2.142(6)
Ag(1)–N(3′)	2.140(6)	Ag(1)–O(1W)	2.490(6)
Ag(2)–N(4)	2.261(6)	Ag(2)–N(4′)	2.242(6)
Ag(2)–O(1^{i})	2.556(7)	Ag(2)–O(3)	2.393(7)
O(1W)···O(1^{ii})	2.779(7)	O(1W)···O(4^{iii})	2.647(7)
O(2W)···O(2^{iv})	2.886(7)	O(2W)···O(4)	2.857(7)
N(3)–Ag1–N(3′)	160.1(2)	N(4)–Ag(2)–N(4′)	154.7(2)

Symmetry relations: i $1 - x, -y, 1 - z$; ii $x, y - 1, z$; iii $1 - x, 1 - y, 1 - z$; iv $2 - x, -y, -z$.

Compound **3**

Ag(1)···Ag(2)	3.089(1)	Ag(1)–N(3)	2.188(8)
Ag(1)–N(4′)	2.351(6)	Ag(1)–O(2W)	2.50(1)
Ag(2)–N(4)	2.274(8)	Ag(2)–N(3′)	2.271(7)
Ag(2)–O(2)	2.18(4)	O(2W)···O(3W)	2.978(9)
O(1W)···O(3)	2.565(9)		
O(2W)···O(3^{i})	2.890(9)		
N(3)–Ag(1)–N(4′)	133.9(2)	N(4)–Ag(2)–N(3′)	122.8(2)
N(3′)–Ag(2)–O(2)	98.2(7)	N(4)–Ag(2)–O(2)	103.0(1)
N(3)–Ag(1)–O(2W)	102.3(3)	N(4′)–Ag(1)–O(2W)	94.4(3)
N(3′)–Ag(2)–N(3$'^{ii}$)	105(1)	N(4′)–Ag(1)–N(4$'^{ii}$)	86.2(6)

Symmetry relations: i $1 + x, y, z$; ii $x, y, 0.5 - z$.

protonation at the N^1 position could be stabilised through formation of intermolecular hydrogen bonds, which is perhaps sterically hindered in the case of the dimethylated derivative. The absorption bands assigned to vibrations of the nitrate group, ν_3 (1380 cm^{-1}) and ν_2 (825 cm^{-1}) for compound **1**, indicate D_{3h} geometry. The IR data for compounds **2**–**4** are in accord with the presence of non-distorted T_d sulfate groups even if the symmetry of these groups in **2** and **3** is lower.

NMR spectroscopy

The ^{1}H and ^{13}C NMR spectra are indicative of complex formation, tp signals appearing downfield shifted with respect to free tp as expected. However, the structural information deduced from ^{1}H NMR spectra is minimal, since the downfield shifts are analogous for the four H atoms present (0.2–0.3 ppm). The ^{13}C NMR resonances, however, appear to be more sensitive to coordination, the N^3, N^4 bridging of the tp moieties appearing to be responsible for the great downfield shift in C^2 and C^7 resonances (3.5–4 ppm). The downfield shift in the C^2 signal can be attributed to its proximity to N^3, whereas, metal binding to N^4 and the resulting charge withdrawal appears to be responsible for an electronic reorganisation in the pyrimidine ring which may eventually result in the observed C^7 deshielding. The shifts in the ^{1}H and ^{13}C NMR signals are significant compared to those of free tp, which may be in accord with an appreciable thermodynamic stability of the complexes in solution.[16] The presence of only one set of signals in solution is indicative that the ligand-exchange rate is very fast on the NMR time-scale and therefore it is not possible to observe in solution the presence of the diverse species found in the solid state (head-to-tail and head-to-head isomers or complexes with two or more bridging ligands).

Conclusion

It should be noted that the stereochemistry of the complexes is very sensible to the preparation conditions and the nature of the anions. It seems that the energetic differences between the different species should be very small and make the final stereochemistry of the system nearly unpredictable. The close approach of the metal atoms in the compounds raises the question of whether the short distance is just the result of the geometrical restraints introduced by the presence of the bridging ligands or is the result of direct metal–metal bonding interactions. The second possibility appears to be gaining stronger support.

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References

1 M. C. Gimeno and A. Laguna, *Chem. Rev.*, 1997, **97**, 511.

2 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *J. Am. Chem. Soc.*, 1995, **117**, 4562.

3 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1895.

4 (*a*) M. A. Romero, J. M. Salas, M. Quiros, M. P. Sanchez, J. Molina and J. El Bahraoui, *J. Mol. Struct.*, 1995, **354**, 189; (*b*) J. M. Salas, M. A. Romero, A. Rahmani and M. Quiros, *An. Quim. Int. Ed.*, 1996, **92**, 249.

5 J. A. R. Navarro, M. A. Romero, J. M. Salas, R. Faure and X. Solans, *J. Chem. Soc., Dalton Trans.*, 1997, 2321.

6 M. Biagini Cingi, A. M. Manotti Lanfredi, A. Tiripicchio, J. P. Cornelissen, J. G. Haasnoot and J. Reedijk, *Inorg. Chim. Acta*, 1987, **129**, 189, 217.

7 E. Kleinpeter, St. Thomas and G. Fischer, *J. Mol. Struct.*, 1995, **355**, 273.

8 SDP, Structure Determination Package, B. A. Frenz & Associates, College Station, TX, 1982.

9 D. L. Smith and H. R. Luss, *Photogr. Sci. Eng.*, 1976, **20**, 184.

10 M. Munakata, M. Maekawa, S. Kitagawa, M. Adachi and H. Masuda, *Inorg. Chim. Acta*, 1990, **167**, 181; T. Tsuda, S. Ohba, M. Takahashi and M. Ito, *Acta Crystallogr., Sect. C*, 1989, **45**, 887; C. Gagnon, J. Hubert, R. Rivest and A. L. Beauchamp, *Inorg. Chem.*, 1977, **16**, 2469.

11 F. A. Cotton, X. Feng, M. Matusz and R. Poli, *J. Am. Chem. Soc.*, 1988, **110**, 7077; D. Fenske, G. Baum, A. Zinn and K. Dehnicke, *Z. Naturforsch., Teil B*, 1990, **45**, 1273; F. Olbrich, B. Zimmer, M. Kastner, C. von Schlabrendorff, G. Vetter and G. Klar, *Z. Naturforsch., Teil B*, 1992, **47**, 1571.

12 A. Bondi, *J. Chem. Phys.*, 1964, **68**, 441.

13 M. Quiros, *Acta Crystallogr., Sect. C*, 1994, **50**, 1236.

14 K. Singh, J. R. Long and P. Stavrapoulos, *J. Am. Chem. Soc.*, 1997, **119**, 2942.

15 U. Siemeling, U. Vorfeld, B. Neumann and H. G. Stammler, *Chem. Commun.*, 1997, 1723.

16 S. Menzer, M. Sabat and B. Lippert, *J. Am. Chem. Soc.*, 1992, **114**, 4644.

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