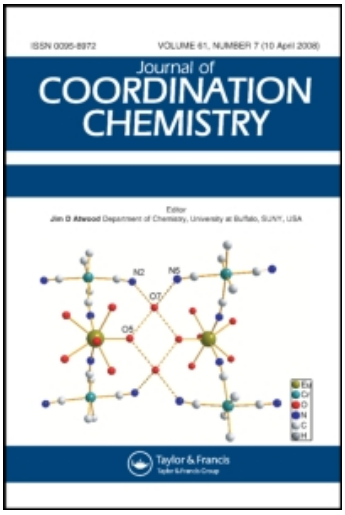

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MIXED DIMETHYLSULFOXIDE-THIOCARBONYL DONOR COMPLEXES OF PLATINUM(II) HALIDES

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The platinum(II) halide adducts *cis*-[Pt(DMSO)(L)X_2], where L = 2,6-dimethyl-4H-pyran-4-thione (DMTP), *N,N*-dimethylthioacetamide (DMTA) or *N,N*-dimethylthioformamide (DMTF) and X = Cl or Br have been prepared and characterized by elemental analysis, by infrared and nmr (^{1}H and ^{13}C) spectroscopy and by thermogravimetric measurements (TG, DTG and DTA). When dissolved in dimethylsulfoxide, the DMTA complexes tend to slowly release the thioamide molecule, whereas the DMTP and DMTF adducts are stable for several weeks, as suggested by the permanence of ^{195}Pt coupling satellites in selected nmr signals.

Keywords: Platinum(II) thioamides, dmso, complexes, properties

INTRODUCTION

Dimethylsulfoxide (DMSO) is widely used as a solvent in cytotoxicity tests of water-insoluble complexes, despite its strong interaction with metal ions. In particular we observed that dimethylsulfoxide removes all ligand molecules in complexes with *N*-disubstituted thiocarbamic esters, as in [Pt(EtOSCNEt_2)$_2X_2$] (X = halide), whereas the *N*-monosubstituted thiocarbamic ester adducts, as [Pt(EtOSCNHMe)$_2X_2$] or [Pt(EtOSCNHMe)$_3$X]X, release all but one ligand molecule in this solvent.[1,2] Because the last complexes have shown a significant cytostatic activity against KB cells when dissolved in dimethylsulfoxide, we have characterized a number of mixed complexes of general formula [Pt(DMSO)(L)X_2] (L = variously substituted thiocarbamic esters).[2,3] It is interesting to observe that those mixed species have a *cis* geometry, which is in favour of activity. Conversely the usual *trans* configuration is preferred in the 1 : 2 platinum halide adducts with thiocarbamic esters.[4]

In the search of platinum halide adducts with thiocarbonyl donors which are stable in dimethylsulfoxide, we extended the study to complexes containing either thioamides or 2,6-dimethyl-4H-pyran-4-thione (DMTP), in which the thiocarbonyl group donor ability is influenced by the aromatic character of the ring. Accordingly, this paper reports the preparation and characterization of the complexes *cis*-[Pt(DMSO)(L)X_2], in which L is DMTP, DMTA (*N,N*-dimethylthioacetamide) or DMTF (*N,N*-dimethylthioformamide) and X is Cl or Br.

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EXPERIMENTAL

Chemicals

N,N-Dimethylthioformamide (DMTF, EGA) and *N,N*-dimethylthioacetamide (DMTA, ICN Biomedicals) were used as supplied. 2,6-Dimethyl-4H-pyran-4-thione (DMTP) was prepared by reaction of 2,6-dimethyl-4H-pyran-4-one and phosphorous pentasulfide in benzene (molar ratio 1 : 1).[5] The solution was treated with water and the benzene layer was separated, dried over anhydrous Na_2SO_4 and evaporated to dryness. Orange DMTP crystals were obtained by recrystallization of the crude product from isopropyl alcohol. Platinum(II) halides were Johnson Matthey products.

Preparation of the Compounds

The complexes have been prepared by reaction of the appropriate platinum halide with a stoichiometric amount of both dimethylsulfoxide and thiocarbonyl ligand in acetone. As an example, the complex *cis*-[Pt(DMSO)(DMTP)Cl_2] was prepared by adding $PtCl_2$ (0.45 mmol) to an acetone solution containing DMTP (0.45 mmol) and DMSO (0.50 mmol; total volume, 4 cm^3). The suspension changed with stirring (2 h) into a red-orange solution and an orange powder, which was filtered, washed with acetone and *n*-pentane and dried *in vacuo*. Yield, 30%. The main fraction of the product was obtained by adding *n*-pentane to the mother solution (red-orange crystals; yield, 55%).

The DMTA and DMTF adducts are almost insoluble in acetone. They have been obtained by stirring a suspension containing the reagents in stoichiometric amounts for *ca* 24 h. The reaction proceeded heterogeneously. The sample purity depends on the purity of the starting platinum halides.

Measurements

Infrared spectra were recorded using Nicolet 5SXC FT-IR and Nicolet 20F far-IR spectrometers (Nujol mulls between KBr and polyethylene discs). ^1H and ^{13}C nmr spectra were obtained using a Jeol FX 90Q spectrometer. Thermogravimetric data in air were obtained with Netzsch STA 429 equipment (flux rate, 250 $cm^3 min^{-1}$; heating rate, 5°C min^{-1}; reference material Al_2O_3).

RESULTS AND DISCUSSION

The complexes (Table 1) have been prepared in acetone by reaction of the appropriate platinum(II) halide with dimethylsulfoxide and thiocarbonyl donor in stoichiometric ratios. Whereas the thioamide adducts are insoluble or slightly soluble in common solvents, the DMTP adducts dissolve in acetone, chloroform and dichloromethane and can be recrystallized from those solvents by addition of *n*-pentane.

Thermogravimetric analyses of all complexes have been performed either in air or dinitrogen. The experimental weight loss values suggest that the final pyrolysis product in air is platinum. In dinitrogen the degradation process is slower, the residue at *ca* 1000°C being probably PtS. As is shown in Figure 1a, decomposition of

TABLE I
Analitycal[a] and infrared[b] data for the complexes.

Compound	Formula	Colour	M.p.(°C)	C%	H%	N%	ν(CN)	DMSO[c]
cis-[Pt(DMSO)(DMTF)]Cl_2	$C_5H_{13}Cl_2NOPtS_2$	yellow	180–4	14.00 (13.86)	3.00 (3.02)	3.41 (3.23)	1592	1128, 1030
cis-[Pt(DMSO)(DMTF)]Br_2	$C_5H_{13}Br_2NOPtS_2$	pinkish-orange	166–9	11.37 (11.50)	2.39 (2.51)	2.68 (2.68)	1591	1128, 1027
cis-[Pt(DMSO)(DMTA)]Cl_2	$C_6H_{15}Cl_2NOPtS_2$	beige	140–2	16.03 (16.11)	3.40 (3.38)	3.06 (3.13)	1564	1131, 1018
cis-[Pt(DMSO)(DMTA)]Br_2	$C_6H_{15}Br_2NOPtS_2$	beige	121–3	13.32 (13.44)	2.78 (2.82)	2.57 (2.61)	1560	1127, 1014
cis-[Pt(DMSO)(DMTP)]Cl_2	$C_9H_{14}Cl_2O_2PtS_2$	orange	170–1	22.12 (22.32)	2.91 (2.91)		1630, 1545[d]	1135, 1026
cis-[Pt(DMSO)(DMTP)]Br_2	$C_9H_{14}Br_2O_2PtS_2$	brown	159–62	19.00 (18.86)	2.49 (2.46)		1630, 1546[d]	1134, 1026

[a] Calculated value in parentheses. [b] Frequencies in cm^{-1}. [c] Dimethylsulfoxide absorptions in the ν(SO) region (see text). [d] DMTP ring vibrations (see text).

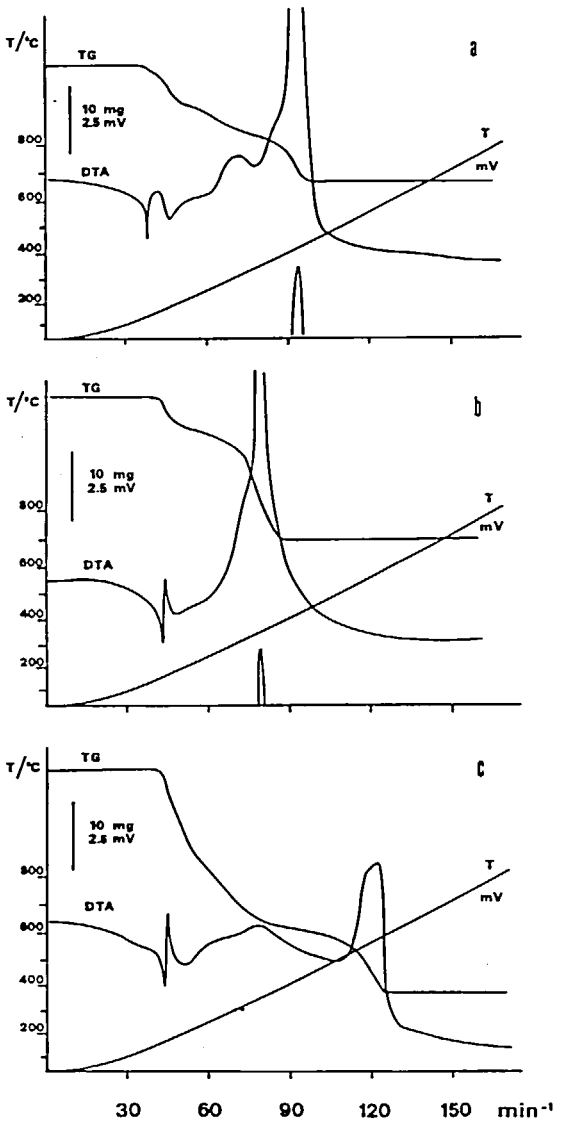

FIGURE 1 Thermograms in air of a: *cis*-[Pt(DMSO)(DMTA)Cl_2] (30.96 mg); b: *cis*-[Pt(DMSO)(DMTP)Cl_2] (36.33 mg); c: *cis*-[Pt(DMSO)(DMTF)Br_2] (51.75 mg).

cis-[Pt(DMSO)(DMTA)Cl_2] in air starts at *ca* 120°C, followed by melting (endotherm at 142°C). The weight loss in the first step (17.7%; endotherm at 190°C) agrees with the calculated value for the release of one DMSO molecule (17.5%). Sample combustion (exotherms at 315°C and 423°C) ends at 465°C, with a total weight loss of 56.5% against a calculated value for platinum as final product of 56.4%. The complex *cis*-[Pt(DMSO)(DMTP)Cl_2] (Figure 1b) melts with decomposition (172°C), the initial weight loss (14.5%; calculated value for evolution of one DMSO molecule,

16.1%) being followed by combustion (exotherm at 360°C) which ends at 440°C (total weight loss, 58.9%; calculated weight loss for platinum, 59.7%). The corresponding bromo-derivative thermograms are similar and confirm that the first decomposition step concerns DMSO release, as observed for various mixed platinum complexes in which the second ligand was a monodentate or bidentate amine.[6,7] Conversely, the DMTF adduct thermograms suggest that halides are involved in the initial degradation process, probably through interaction with the CH hydrogen. In fact, *cis*-[Pt(DMSO)(DMTF)Br_2] (Figure 1c) melts with decomposition at 172°C. The weight loss up to 400°C (*ca.* 45%) compares well with release of DMSO + 2Br (45.6%); the related values for the analogous chloro-derivative were: found, 33.8%; calculated for release of DMSO + 2Cl, 34.4%). The final pyrolysis temperature (600°C) is higher than that of the DMTA and DMTP adducts, the total weight loss being 63.2% (calculated for platinum, 62.6%).

In the 1650–1500 cm^{-1} spectral region the DMTA and DMTF adducts show strong absorption due to the C–N bond stretch of the coordinated ligand (Table I). The ν(CN) in free ligands occur at 1540 cm^{-1}(DMTF) and 1510 cm^{-1}(DMTA) and shift to higher energies on coordination, as expected for *S*-bound moieties. In this region the infrared spectrum of DMTP contains a strong band at 1641 cm^{-1} and a medium one at 1559 cm^{-1}, assigned to ring vibrations as for the analogous species 2,6-dimethyl-4H-pyran-4-one (DMP).[8] On coordination these bands shift to low energy (at 1630 cm^{-1} and 1545 cm^{-1} respectively), as observed for various lanthanide-DMP complexes.[9] The free DMTP ν(CS) absorption (1095 cm^{-1}) is nearly unchanged in the complexes. The infrared spectra below 550 cm^{-1} (Table II) are consistent with the *cis* geometry of the adducts. As for the analogous mixed complexes with thiocarbamic esters, the spectra contain two bands assignable to Pt-halid vibrations, in the 330–300 cm^{-1} range for the chloro-derivatives and in the 225–200 cm^{-1} range for the bromo-analogues. The two medium bands at *ca* 440 cm^{-1} and 375 cm^{-1}, common to all complexes, are due to the symmetric and asymmetric stretch of the CSO group in coordinated DMSO, respectively. As for the parent thiocarbamic ester mixed complexes, the thioamide and DMTP adducts give two medium absorptions in the dimethylsulfoxide S = O stretch region, at *ca* 1130 cm^{-1} and 1030 cm^{-1} (Table 1). The general criterion to distinguish *S*-bound from *O*-bound DMSO (shift of free dimethylsulfoxide S = O absorption at 1055 cm^{-1} to higher and lower energies respectively)[2,3] does not seem to hold for those mixed complexes in which DMSO is surely *S*-bound.

Proton nmr data for ligands and complexes are given in Table III. The thioamide molecules are planar, owing to the barrier to rotation around the C–N bond, of the order of 100 kJ mol^{-1}.[10] Consequently DMTF and DMTA give two equally intense signals for the non-equivalent methyl groups bound to nitrogen, the CH and CCH_3 proton singlets being observed at 9.16 ppm and 2.62 ppm, respectively. On coordination a downfield shift of the signals is observed, which is more marked for the CH and CCH_3 protons. The DMTF complexes are scarcerly soluble in deuterated chloroform and, despite numerous transients being collected, it is difficult to observe the CH signal satellites due to proton-^{195}Pt coupling. These satellites are instead evident in the spectra in deuterated dimethylsulfoxide, in which the DMTF adducts are quite soluble. The spectra of aged (2–3 weeks) solutions of DMTF adducts in deuterated dimethylsulfoxide are unchanged, whereas in the analogous DMTA complexes the ligand signals broaden with time, indicating slow DMTA release. The proton nmr spectrum of DMTP contains the singlets due to the methyl (2.18 ppm) and ring CH (6.93 ppm) protons. In the complexes both signals are shifted downfield,

TABLE II
Infrared data for the complexes (550–150 cm^{-1}).[a]

cis-[Pt(DMSO)(DMTF)]Cl_2	519w		444ms	399m	367m	*326, 311*s	276vw	232vw		143mw
cis-[Pt(DMSO)(DMTF)]Br_2	518w		441ms	398m	368m		272w		*218, 211*m	150mw
cis-[Pt(DMSO)(DMTA)]Cl_2	535w	498vw	442ms	429sh	379m	*329, 308*s	284w	254vvw	242vvw	169mw
cis-[Pt(DMSO)(DMTA)]Br_2	534w	496w	438ms	429sh	375m	325vw	278w	247vw	*222, 204*m	168vvw
cis-[Pt(DMSO)(DMTP)]Cl_2	542sh 538vvw	476vw	441m	433wsh	374mw 364sh	*327, 304*s	275wbr	231vvw	202mw	168vw
cis-[Pt(DMSO)(DMTP)]Br_2	538vw	475vvw	439m	431wsh	375mw 361sh		273wbr	232vvw	*215, 209*m	200sh 181vvw 169vvw

[a] Platinum-halide stretching frequencies are given in italics.

TABLE III

^{1}H nmr data for ligands and complexes (ppm; T *ca* 25°C).[a]

Compound	NMe_2	C(S)R	Me_2SO
DMTA[b]	3.46, 3.28	2.62	
cis-[Pt(DMSO)(DMTA)Cl_2][b]	3.49, 3.38	3.10	3.49 (22.5)
cis-[Pt(DMSO)(DMTA)Cl_2][c]	3.38, 3.32br	2.97br	2.51[d]
cis-[Pt(DMSO)(DMTA)Br_2][b]	3.49, 3.38	3.07	3.55 (22.9)
cis-[Pt(DMSO)(DMTA)Br_2][c]	3.39, 3.32br	2.95br	2.51[d]
DMTF[b]	3.27, 3.24	9.16	
cis-[Pt(DMSO)(DMTF)Cl_2][b]	3.39, 3.29	9.73	3.55 (22.9)
cis-[Pt(DMSO)(DMTF)Cl_2][c]	3.43, 3.22	9.53 (54.7)	2.51[d]
cis-[Pt(DMSO)(DMTF)Br_2][b]	3.54, 3.42	9.86	3.60 (23.4)
cis-[Pt(DMSO)(DMTF)Br_2][c]	3.41, 3.20	9.52 (56.2)	2.51[d]
	CH	CH_3	
DMTP[b]	6.93	2.18	
cis-[Pt(DMSO)(DMTP)Cl_2][b]	7.65	2.39	3.48 (23.4)
cis-[Pt(DMSO)(DMTP)Cl_2][c]	7.78	2.46	2.51[d]
cis-[Pt(DMSO)(DMTP)Br_2][b]	7.63	2.39	3.55 (23.0)
cis-[Pt(DMSO)(DMTP)Br_2][c]	7.76	2.45	2.51[d]

[a] The ^{195}Pt coupling values (Hz) are in parentheses. [b] In $CDCl_3$. [c] In deuterated dimethylsulfoxide. [d] Free dimethylsulfoxide.

the effect being more marked for the CH resonance. In deuterated chloroform all complexes show the DMSO proton singlet at *ca* 3.55 ppm, with proton-^{195}Pt coupling of *ca* 23 Hz. The good solubility of the DMTP adducts allows recording of ^{13}C nmr spectra (Table IV). On coordination CS and CH carbon signals, at 201.8 ppm and 124.5 ppm in the free ligand, ^{11}shift upfield and show the satellites due to ^{195}Pt coupling. Conversely, the resonance of the ring carbon atoms bound to oxygen shifts slightly downfield, whereas the methyl carbon signal is nearly unchanged. The DMSO carbon resonance is observed at *ca* 46 ppm, downfield with respect to free DMSO (40.6 ppm), as expected for coordination through sulfur.[12] Nmr spectra of the DMTP adducts in deuterated dimethylsulfoxide indicate that solvent does not remove DMTP from the platinum coordination sphere, as with the DMTF adducts.

TABLE IV

^{13}C nmr data for DMTP and complexes (ppm; T *ca* 25°C).[a]

Compound	CS	COC	CH	CH_3	Me_2SO
DMTP[b]	201.8	158.9	124.5	19.2	
cis-[Pt(DMSO)(DMTP)Cl_2][b]	188.7 (35.2)	163.7	120.4 (74.2)	20.0	45.4 (60.5)
cis-[Pt(DMSO)(DMTP)Cl_2][c]	187.1 (39.1)	165.4	119.5 (74.2)	19.5	d
cis-[Pt(DMSO)(DMTP)Br_2][b]	188.5 (37.1)	163.5	120.4 (74.2)	20.0	46.3 (64.4)
cis-[Pt(DMSO)(DMTP)Br_2][c]	186.5 (39.4)	165.3	119.3 (74.2)	19.5	d

[a] The ^{195}Pt coupling values (Hz) are in parentheses. [b] In $CDCl_3$. [c] In deuterated dimethylsulfoxide. [d] Free dimethylsulfoxide by solvent exchange.

REFERENCES

1. A. Furlani, V. Scarcia, G. Faraglia, L. Sindellari and B. Zarli, *Inorg. Chim. Acta*, **67**, L41 (1982).
2. G. Faraglia, F. Barbaro and L. Sindellari, *Transition Met. Chem.*, **12**, 457 (1987) and references therein.
3. G. Faraglia and F. Barbaro, *J. Coord. Chem.*, **19**, 349 (1989), and references therein.
4. G. Faraglia, L. Sindellari, B. Zarli and I. Agnoletti, *Inorg. Chim. Acta*, **58**, 13 (1982).
5. M. Yamamoto, S. Iwesa, K. Takatsuki and K. Yamada, *J. Org. Chem.*, **51**, 346 (1986).
6. J.A. Davies and G.A. Miller, *Thermochim. Acta*, **62**, 35 (1983).
7. E.A. Andronov, Yu. N. Kukushkin, T.M. Lukicheva, V.P. Kotel'nikov and Yu. S. Shcherbakov, *Russ. J. Inorg. Chem.*, **21**, 1632 (1976).
8. A.R. Katritzky and R. Alan Jones, *Spectrochim. Acta*, **17**, 64 (1961).
9. S. Sitran, D. Fregona and G. Faraglia, *J. Coord. Chem.*, **20**, 193. (1989).
10. T.H. Siddal III, W.E. Stewart and F.D. Knight, *J. Phys. Chem.*, **74**, 3580 (1970).
11. I.W.J. Still, N. Plavac, D.M. McKinnon and M.S. Chauhan, *Can. J. Chem.*, **54**, 280 (1976).
12. J.D. Fotheringham, G.A. Heath, A.J. Lindsay and T.A. Stephenson, *J. Chem. Res. (S)*, 82 (1986).