COS Trapping by Palladium Pyrazolates: Addition *vs.* Clathration

Norberto Masciocchi,*[a] Massimo Moret,[a] Angelo Sironi,[a] G. Attilio Ardizzoia,*[b] Sergio Cenini[b] and Girolamo La Monica†[b]

[a] *Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, via G. Venezian 21, 20133 Milano, Italy*

[b] *Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Milano, via G. Venezian 21, 20133 Milano, Italy*

[{Pd(dmpz)$_2$(Hdmpz)$_2$}$_2$] (Hdmpz = 3,5-dimethylpyrazole) reacts with COS, both in solution and in the solid state, affording [Pd{SC(O)dmpz}$_2$] and [{Pd(dmpz)$_2$(Hdmpz)$_2$}$_2$]·COS, respectively; the structure of the latter is determined by *ab initio* methods from conventional X-ray powder diffraction data only.

The activation of simple heterocumulene fragments, such as CO_2 and its heavier congeners, by transition metal complexes has received in the past decade a great deal of attention, in search for cheap C_1 sources.[1] For these molecules, a number of different coordination modes and chemical transformations has been discovered.[2]

During a systematic study of the chemical reactivity of the recently characterized[3] [{Pd(dmpz)$_2$(Hdmpz)$_2$}$_2$] dimer **1**, we found that it reacts rapidly, in CH_2Cl_2 solution at room temp. with a number of heterocumulenes, such as CS_2, COS and OCNR (R = *p*-tolyl). By reaction of **1** with COS, crystals of [Pd{SC(O)dmpz}$_2$] **2** were isolated and studied by X-ray diffraction,‡ showing that monomeric, centrosymmetric molecules, containing a square-planar *trans*-PdN_2S_2 chromophore, are formed (see Fig. 1). Differently from the η^1-SC(O)NR_2 or chelating η^1-S,η^1-O coordination mode of all structurally characterized monothiocarbammato ligands, but accordingly with the soft nature of S and Pd and the coordination model put forward by Trofimenko,[4] in **2** chelating η^1-S,η^1-N coordination occurs and the exocyclic carbonyl fully retains its double bond character [ν_{CO} at 1658 cm^{-1}, C–O 1.200(6) Å].

With the aim of freezing out the reaction mechanism and in order to isolate a coordinated, not yet functionalized, COS fragment, we suspended solid, polycrystalline [{Pd(dmpz)$_2$(Hdmpz)$_2$}$_2$] **1** in liquid COS at −78 °C under magnetic stirring; under these conditions, it transformed quantitatively into a white powder **3**, later formulated from thermogravimetric and diffraction analyses, as [{Pd(dmpz)$_2$(Hdmpz)$_2$}$_2$]·COS. This compound is moderately stable if stored under nitrogen at −18 °C and shows a strong, sharp (see Fig. 2) ν_{as}(SCO) IR absorption at 2045 cm^{-1} [initially attributed to the still elusive η^1 coordination mode, paralleling similar claims[1,2,5] on the CO_2 and CS_2 congeners; ν_{as}(SCO) of free COS = 2062 cm^{-1} (ref. 2)], which is rapidly lost at room temp. ($t_{1/2}$ few hours). Repeated attempts to grow single crystals of this species failed. Therefore, the structural characterization was performed using *ab initio* X-ray powder diffraction (XRPD) methods, which, in the recent past, have been shown to be a viable technique for assessing the crystal and molecular structures of a number of molecular and/or polymeric materials not available as single crystals of suitable quality.[6]

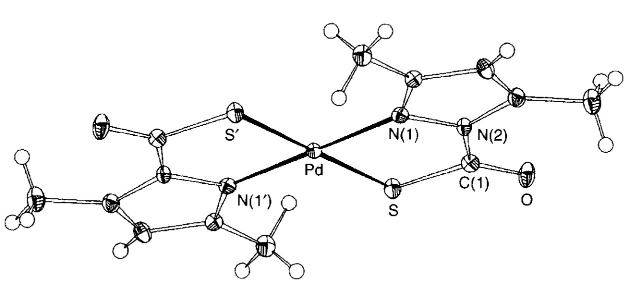

Fig. 1 ORTEP plot of the [Pd(SC(O)dmpz)$_2$] molecule. Thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (°): Pd–S 2.305(1), Pd–N 2.051(4), S–C 1.721(5), C–O 1.200(6) and N–Pd–S 83.6.

Room temp. XRPD studies of **3** showed§ that the identity of the [{Pd(dmpz)$_2$(Hdmpz)$_2$}$_2$] molecule is essentially retained [Pd···Pd 3.746(1) and 3.748(6) Å, in **1** and **3**, respectively] while COS molecules are hosted in the crystal lattice as non-bonded fragments, the shortest Pd–(COS) distance being Pd···C (*ca.* 5.06 Å, see Fig. 3). COS molecules are disordered about the fourfold crystallographic {and, for [{Pd(dmpz)$_2$(Hdmpz)$_2$}$_2$], molecular} axis of the tetragonal *I*422 space group. The proposed model is also consistent with the fact that solid [{M(pz)$_2$(Hpz)$_2$}$_2$] (M = Pd, Pt; Hpz = pyrazole), known to be isostructural but not isomorphous with **1**, do not react with liquid COS, as if this 'reaction' were controlled by crystal lattice, rather than molecular, features. Accordingly, [{Pt(dmpz)$_2$(Hdmpz)$_2$}$_2$], which we proved by XRPD to be isomorphous with **1**, 'absorbs' COS but generates a labile adduct, as monitored by IR [ν_{as}(SCO) 2043 cm^{-1}, $t_{1/2}$ few minutes].

The stereochemical transformation of the host lattice from centric *C*2/*c* of **1**, containing a racemate of chiral [{Pd(dmpz)$_2$(Hdmpz)$_2$}$_2$] molecules of idealized 422 (D_4) symmetry, to the acentric *I*422 space group requires spontaneous resolution of the enantiomeric moieties, which, despite of a simple topological relation between the two lattices, can

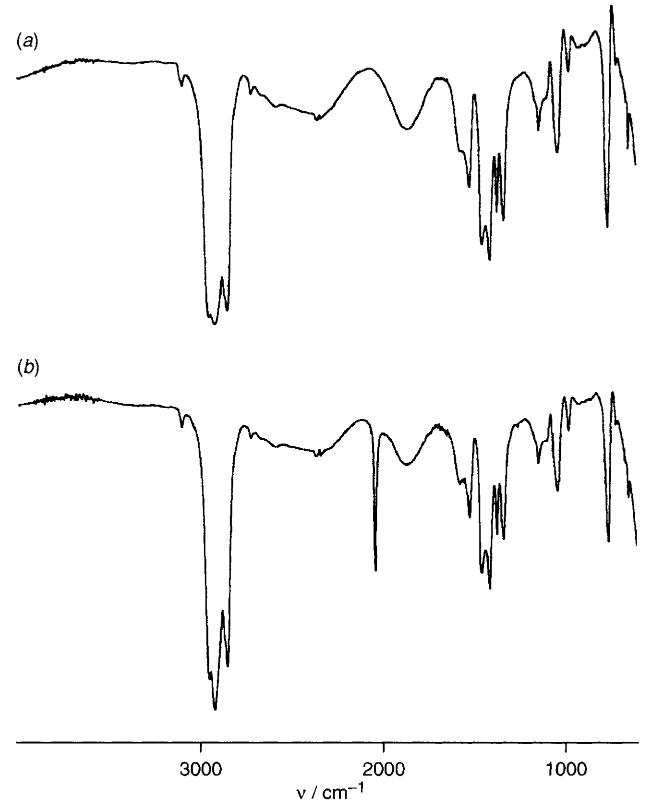

Fig. 2 Infrared absorption spectra of (*a*) **1** and (*b*) **3** (Nujol mulls, 4000–600 cm^{-1})

only be interpreted by the presence of two subsequent steps, *i.e.* dissolution of **1** into liquid COS and recrystallization of **3**, as a conglomerate of enantiomorphic crystals. The intramolecular process of reversing the chirality of (half of) the molecules of **1** by simultaneous breaking of four strong hydrogen bonds and cooperative rotation of eight Hdmpz/dmpz ligands about the Pd–N axes is ruled out by energetic considerations and solution ^{1}H NMR spectra.[3]

On losing COS, **3** smoothly transforms into **4**, which, showing the same structure of **3** (with a 1.1% shorter c axis), also contains enantiomorphic crystals of a new polymorph of $[\{Pd(dmpz)_2(Hdmpz)_2\}_2]$.[¶] For the reasons outlined above, the original lattice of **1** cannot be restored by loss of COS; this acts therefore as a further proof of the non-innocent character of liquid COS in the formation of **3**, excluding simple gas/solid diffusion.

The reported XRPD structure determination of compound **3**, which only exists as a solid (poly)crystalline phase, shows, *inter alia*, that the above-mentioned IR band must be attributed to clathrated, rather than η^1 coordinated, COS molecules, shedding new light onto the possible misinterpretation of spectroscopic bands in assigning this still structurally uncharacterized coordination mode of carbonyl sulfide and of its congeners.

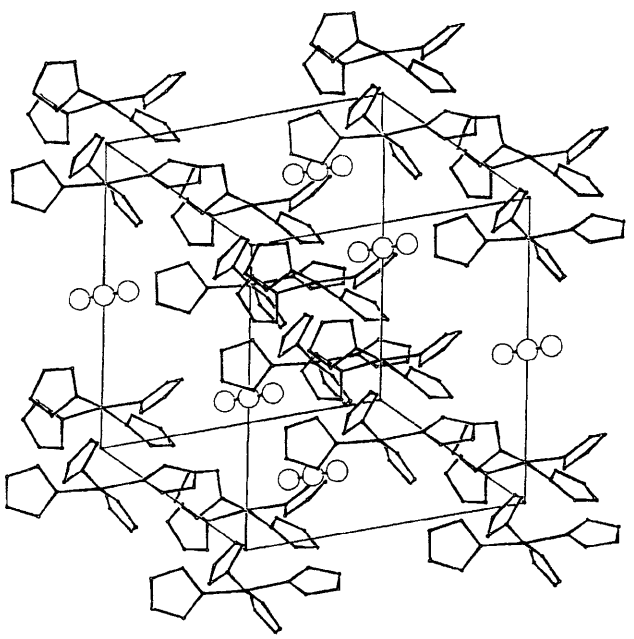

Fig. 3 Unit cell diagram of $[\{Pd(dmpz)_2(Hdmpz)_2\}_2]\cdot COS$, showing clathrated, uncoordinated COS molecules. Only one orientation of the disordered COS molecules (see text) is depicted. Hydrogen and methyl carbon atoms are omitted for clarity.

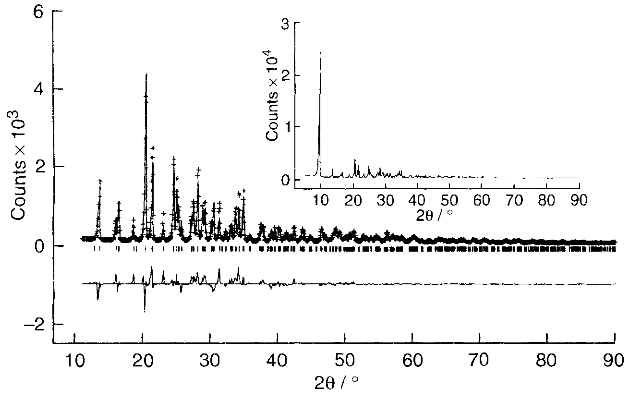

Fig. 4 Rietveld refinement plot for **3** (11 ⩽ 2θ ⩽ 90°). Reflection markers and difference plot at the bottom. The insert shows the full raw data.

Despite the failure to stabilize the reaction intermediate of the formation of **2** within the crystal lattice, XRPD alone allowed a ‘strong’ chemical belief to be discarded and lead to the proposal of a different structural model for **3**, thus proving to be a convenient tool for validating or rejecting structural hypotheses.

This project was supported by the Italian MURST (40%) and CNR (Progetto Finalizzato Chimica Fine II). We thank Mr G. Mezza for technical support.

Received, 3rd July 1995; Com. 5/04283F

Footnotes

[†] On leave from Istituto di Scienze Matematiche, Fisiche e Chimiche, Università di Milano, via Lucini 3, 22100 Como, Italy.

[‡] *Crystal data* for $[Pd\{SC(O)dmpz\}_2]$ **2**: $C_{12}H_{14}N_4O_2PdS_2$, monoclinic, space group $P2_1/c$, $a = 4.0503(5)$, $b = 13.717(1)$, $c = 12.943(2)$ Å, $\beta = 93.05(2)°$, $U = 718.1(3)$ Å^3, $Z = 2$, $M_r = 416.76$, $D_c = 1.928$ g cm^{-3}, $\mu = 15.63$ cm^{-1}, $F(000) = 416$. The structure was solved from single-crystal diffraction data, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), and Patterson and difference Fourier methods. Final R and $wR2$ values for 1247 observed reflections $[F^2 > 4\sigma(F^2)]$ were 0.032 and 0.060, respectively.

[§] *Crystal data* for $[\{Pd(dmpz)_2(Hdmpz)_2\}_2]\cdot COS$ **3**: (freshly prepared) $C_{41}H_{60}N_{16}OPd_2S$, tetragonal, space group $I422$, $a = 13.151(3)$, $c = 13.969(6)$ Å, $U = 2416(2)$ Å^3, $Z = 2$, $M_r = 1037.91$, $D_c = 1.427$ g cm^{-3}, $\mu = 69.36$ cm^{-1}, $F(000) = 1068$. The structure was solved from powder diffraction data (graphite-monochromated Cu-Kα radiation), using TREOR[7] $[M(24) = 20$, $F(24) = 41$ (0.009, 63)] for indexing, LeBail's method[8] of integrated intensity extraction, Patterson synthesis (which allowed the location of the metal atoms), difference Fourier and model building techniques, and refined by the Rietveld method, using GSAS.[9] Final R_p, R_{wp} and R_F values, for 3951 data points (650 reflections) observed in the range $11 \leqslant 2\theta \leqslant 90°$, are 0.12, 0.16 and 0.08, respectively (8 h run). Experimental and computational details can be found in related papers, such as ref. 6. A plot of the observed and calculated powder patterns is shown in Fig. 4. Any attempt of refining a centric (possibly disordered) tetragonal model resulted in much poorer data fitting. Note that, owing to the loss of COS during the data collection period, the ‘refined’ lattice parameters are different from those reported above; of even greater importance, they change slightly during the experiment: therefore, an empirical correction has been considered. The ‘final’ occupancy of the COS molecule can be estimated to be *ca.* 40%.

For **2** and **3**, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

[¶] *Crystal data* for tetragonal $[\{Pd(dmpz)_2(Hdmpz)_2\}_2]$ **4**: $C_{40}H_{60}N_{16}Pd_2$, space group $I422$, $a = 13.133(2)$, $c = 13.816(2)$ Å, $U = 2383(1)$ Å^3, $Z = 2$, $M_r = 977.83$, $D_c = 1.363$ g cm^{-3}, $\mu = 65.87$ cm^{-1}, $F(000) = 1008$.

References

1 A. Behr, *Carbon Dioxide Activation by Metal Complexes*, VCH, Weinheim, 1988.
2 P. V. Yaneff, *Coord. Chem. Rev.*, 1977, **23**, 183; K. K. Pandey, *Coord. Chem. Rev.*, 1995, **140**, 37.
3 G. A. Ardizzoia, G. La Monica, S. Cenini, M. Moret and N. Masciocchi, submitted.
4 S. Trofimenko, *J. Org. Chem.*, 1968, **33**, 890.
5 D. Commereue, I. Doueck and G. Wilkinson, *J. Chem. Soc. A*, 1970, 1771; F. G. Moers, R. W. M. ten Hoedt and J. P. Langhout, *Inorg. Chem.*, 1973, **12**, 2196.
6 See for example: N. Masciocchi, M. Moret, P. Cairati, A. Sironi, G. A. Ardizzoia and G. La Monica, *J. Am. Chem. Soc.*, 1994, **116**, 7768.
7 P. E. Werner, L. Eriksson and M. Westdahl, *J. Appl. Crystallogr.*, 1985, **18**, 367.
8 A. Le Bail, H. Duroy and J. L. Fourquet, *Mat. Res. Bull.*, 1988, **23**, 447.
9 A. C. Larson and R. B. Von Dreele, LANSCE, Ms-H805, Los Alamos National Laboratory, NM, USA, 1990.