A Sulphur Monoxide-bridged Dinickel A-frame Complex: $[Ni_2(\mu\text{-}SO)(PPh_2CH_2PPh_2)_2Cl_2]$

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Direct oxidative addition of thionyl chloride ($SOCl_2$) to a nickel(0) complex is an unprecedented procedure for the preparation of sulphur monoxide complexes of the type $[Ni_2(\mu\text{-}SO)(PPh_2CH_2PPh_2)_2Cl_2]$ in which the μ-SO group was found by an *X*-ray structural study to be tilted with respect to the Ni–Ni vector.

Sulphur monoxide is unstable and generally rapidly disproportionates to S_2O and SO_2, but it is an important intermediate in sulphur oxide chemistry. The use of transition metal complexes to trap sulphur monoxide has received considerable attention.[1] It may bond to transition metals in several modes including 4-centre-2-electron as in $[Fe_3(CO)_9(\mu_3\text{-}SO)]$,[2] 2-centre-2-electron as in $[IrCl(SO)(PR_3)_2]$,[3] or 3-centre-4-electron or 3-centre-2-electron as in several dinuclear transition-metal complexes.[4,5]

We report here the synthesis and structural characterization of a new dinickel μ-SO 'A-frame' complex. The complex $[Ni_2(\mu\text{-}SO)(dppm)_2Cl_2]$ was obtained by the reaction of $[Ni(cod)_2]$[6] with dppm [cod = cyclo-octa-1,5-diene; dppm = bis(diphenylphosphino)methane] and thionyl chloride (2:2:1) in toluene. The mixture was stirred for 30 min at −20 °C under nitrogen. A green precipitate ($NiCl_2$) which formed initially was filtered off. Diethyl ether was then added to the filtrate to produce a purple crystalline solid in 20—25% yield, IR(KBr) ν (S=O) 966s cm^{-1}. The ^1H NMR (CD_2Cl_2) data indicate that all four methylene protons in dppm are inequivalent: δ 2.00, 2.22, 3.42, and 4.05 (each m, 1 H), indicating an asymmetric or tilted SO moiety.[5] The $^{31}P\{^1H\}$ NMR (CH_2Cl_2, 85% H_3PO_4 external) spectrum consists of an AA'BB' spin system centred at δ 10.5 ppm.

X-Ray-quality crystals were obtained by slow diffusion of diethyl ether into a methylene chloride solution. The structure of the title complex is presented in Figure 1.‡ Generally, dinuclear nickel complexes are found to possess 'cradle'[7] or 'mixed geometry,' pseudo-tetrahedral/pseudo-square-planar structures.[8] The title complex is one of the few nickel 'A-frame' complexes reported to date.[9] The Ni(1)–Ni(2) distance is 3.308(1) Å, which clearly indicates the absence of a direct Ni–Ni bond. The structure reveals two different tilt geometries of the SO oxygen atom. The occupancy factors for the oxygen atom disorder were refined to 0.75 O(a) and 0.25 O(b). The bond distances between S–O(a) and S–O(b) are 1.459(7) and 1.44(1) respectively. Selected bond angles are listed in Figure 1.

The title complex represents the first example of the direct formation of sulphur monoxide *via* oxidative addition of $SOCl_2$. Several μ-S and μ-SO_2 A-frame species of the platinum group metals have been reported. James and co-workers

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‡ *Crystal data* for $C_{50.69}H_{45.37}Cl_{3.37}Ni_2OP_4S$: M_r = 1063.38, space group $P2_1/c$, a = 16.706(2), b = 11.615(3), c = 25.546(2) Å, β = 101.576(8)°, U =4855(2) Å^3, Z = 4, μ = 11.76 cm^{-1}. The structure was solved by SHELX-86. The remaining atoms were located using DIRDIF and successive least squares/difference Fourier synthesis. The structure was refined to R = 0.042 and R_w = 0.051 for 3782 observations with $I > 3\sigma(I)$ with Mo-K_α radiation. Data were corrected for absorption empirically, μ = 11.76 cm^{-1}. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

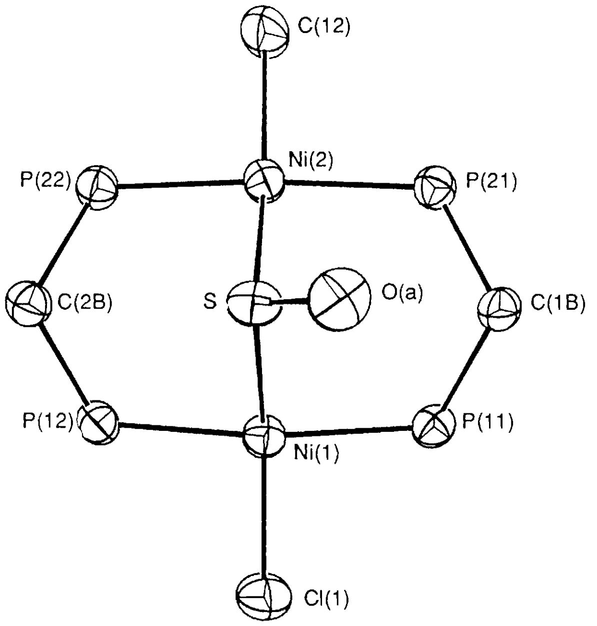

Figure 1. ORTEP drawing of $[Ni_2(\mu\text{-}SO)(dppm)_2Cl_2]$ without dppm phenyl rings and hydrogen atoms. The atoms are depicted as 50% probability ellipsoids. Important bond distances (Å) and angles (°): Ni(1)–Ni(2), 3.308(1); Ni(1)–Cl(1), 2.235(2); Ni(2)–Cl(2), 2.224(2); Ni(1)–S, 2.127(2); Ni(1)–P(11), 2.227(2); Ni(2)–S, 2.130(2); S–O(a), 1.459(7); S–O(b), 1.44(1); Cl(1)–Ni(1)–S, 159.66(7); P(11)–Ni(1)–P(12), 161.32(7); Cl(2)–Ni(2)–S, 163.33(8); P(21)–Ni(2)–P(22), 169.54(8); Ni(1)–S–Ni(2), 101.98(7); Ni(1)–S–O(a), 113.9(3); Ni(1)–S–O(b), 117.5(6); Ni(2)–S–O(a), 114.0(3); Ni(2)–S–O(b), 119.1(b); O(a)–S–O(b), 90.9(7).

reported the structural characterization of a μ-SO intermediate, $Pd_2(\mu\text{-}SO)Cl_2(dppm)_2$, in the *m*-chloroperbenzoic acid oxidation of $[Pd_2(\mu\text{-}S)Cl_2(dppm)_2]$ to $[Pd_2(\mu\text{-}SO_2)Cl_2(dppm)_2]$.[5,10] The tilted 3-centre-2-electron μ-SO bonding mode evident in the structure of the title complex and overall A-frame structure are qualitatively similar to these features in the palladium complex.[5] The structural similarities between the Pd and Ni complexes are surprising in view of the fact that Ni 'A-frame' complexes are in general quite scarce. In the case of nickel, the stability of the μ-SO complex appears to be unique. Preliminary reactivity studies suggest that both phosphine reduction and trimethylamine *N*-oxide oxidation of $[Ni_2(\mu\text{-}SO)(dppm)_2Cl_2]$, in attempts to prepare μ-S and μ-SO_2 species respectively, led instead to unstable, inseparable materials.

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