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Molecular Zinc Oxide and Sulfide Complexes stabilized by Pyrazolylborate Ligands

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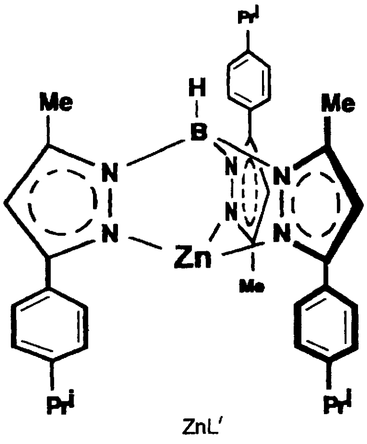
The highly encapsulating tris(3-*p*-cumenyl-5-methylpyrazolyl)borate L and its isomer L′ have been found to create sufficient steric hindrance and electronic saturation to stabilize non-oligomeric Zn–O–Zn and Zn–S–Zn units in the neutral dinuclear complexes $[(L'Zn)_2O]$ and $[(LZn)_2S]$, the crystal structures of which were determined.

Oxide and sulfide are commonplace as counter ions in purely inorganic transition-metal compounds. In co-ordination chemistry they occur mainly in the oxo and thio complexes of high-valent metals. Co-ordination compounds of the low-valent metals with oxide and sulfide are generally oligomeric, and simple dinuclear species $(L_nM)_2O$ and especially $(L_nM)_2S$ are rarities, even in the well investigated fields of iron[1] or molybdenum[2] chemistry. Specifically for zinc, we are not aware of any such organometallic or co-ordination compounds. Furthermore, we did not succeed in finding any other pairs of dinuclear transition-metal compounds $(L_nM)_2O$ and $(L_nM)_2S$ for which both structures have been determined.

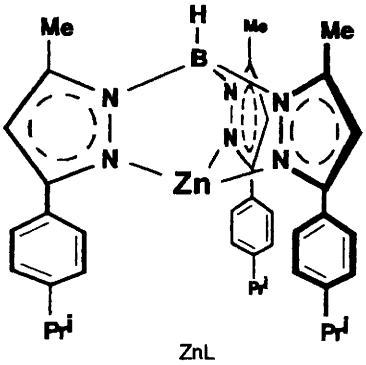
Resulting from a long-standing interest in this type of chemical species[3,4] we have now tried to obtain molecular $(LZn)_2O$ or $(LZn)_2S$ complexes. We found that the uninegative, highly encapsulating pyrazolylborate L[5] provides the metal with a suitable electronic and steric environment for this purpose, thereby allowing the synthesis of compounds **1** and **2** in a simple manner.

The oxide **1**[†] was obtained accidentally during our investigations of the hydroxide complex [ZnL(OH)].[5] The NMR spectra had indicated that compound L contained an impurity. The conversion of L into the hydroxide complex [ZnL(OH)] *via* addition of $Zn(ClO_4)_2{\cdot}6H_2O$ and KOH allowed the presumed impurity to be separated from the main product by crystallization from methanol. The compound thus isolated in less than 1% yield was **1**. This leads us to assume that the impurity of L is its unsymmetrical isomer L′, in accordance with observations by Trofimenko and co-workers[6] of similar pyrazolylborates with voluminous substituents. The synthetic pathway then suggests that [ZnL′(OH)] is an intermediate in the spontaneous formation of **1** although we have no proof for its existence.[‡]

Fig. 1 shows the molecular structure of compound **1**.[§] The molecules of **1** are centrosymmetric with the oxygen atoms at the crystallographic inversion centres. This would imply linearity of the Zn–O–Zn unit, however the significant elong-



L′Zn–O–ZnL′ **1**



LZn–S–ZnL **2**

[†] To KL (2.00 g, 3.08 mmol) dissolved in CH_2Cl_2 (50 cm^3) was added $Zn(ClO_4)_2{\cdot}6H_2O$ (1.15 g, 3.08 mmol) dissolved in methanol (20 cm^3) and KOH (0.17 g, 3.08 mmol) dissolved in methanol (10 cm^3). Filtration from $KClO_4$ and repeated crystallization to remove [ZnL(OH)] yielded compound **1** (13 mg). ^1H NMR ($CDCl_3$): δ 0.79 (d, 24 H, J^3 6.9), 1.36 (d, 12 H, J^3 6.9), 2.32 (s, 12 H), 2.60 (spt, 4 H, J^3 6.9), 2.63 (s, 6 H), 3.05 (spt, 2 H, J^3 6.9), 6.12 (s, 2 H), 6.26 (s, 4 H), 6.68 (d, 8 H, J^3 8.2), 7.00 (d, 8 H, J^3 8.2), 7.31 (d, 4 H, J^3 8.2) and 7.39 (d, 4 H, J^3 8.2 Hz).

[‡] We have not succeeded in isolating L′ or [ZnL′(OH)] yet. Thermal treatment of the isomer mixtures of L and L′ or of pure L did not lead to a change in the quantity of L′. Furthermore, thermolysis of pure [ZnL(OH)] caused no reaction until decomposition set in at *ca.* 200 °C, and spectroscopic analysis of the decomposition compounds did not indicate the formation of L′, compound **1**, or [LZn–O–ZnL].

[§] Crystal data: $C_{78}H_{92}B_2N_{12}OZn_2{\cdot}2CH_3OH$ **1**, $M = 1430.2$, crystal dimensions 0.5 × 0.3 × 0.3 mm, monoclinic, space group $C2/c$, $a = 23.293(14)$, $b = 13.369(3)$, $c = 26.745(8)$ Å, $\beta = 104.61(4)°$, $U = 8059(6)$ Å^3, $Z = 4$, $D_c = 1.18$ g cm^{-3}, $\mu = 6.5$ cm^{-1}, $F(000) = 3032$, $2\theta \leqslant 46°$, Mo-Kα radiation (λ 0.710 69 Å), Nonius-Turbo-CAD4 diffractometer. The structure was solved by direct methods and refined anisotropically (SHELXS 86[7] and SHELXL 93[8]): 5568 reflections, 440 parameters, $R1 = 0.079$. $C_{78}H_{92}B_2N_{12}SZn_2$ **2**, $M = 1382.1$, 0.6 × 0.3 × 0.3 mm, monoclinic, space group $P2_1/n$, $a = 21.114(2)$, $b = 15.378(1)$, $c = 23.424(2)$ Å, $\beta = 105.23(1)°$, $U = 7338(1)$ Å^3, $Z = 4$, $D_c = 1.25$ g cm^{-3}, $\mu = 7.3$ cm^{-1}, $F(000) = 2920$, $2\theta \leqslant 50°$, radiation and diffractometer as for **1**. The structure was solved and refined as before: 12 738 reflections, 856 parameters, $R1 = 0.055$. Further details of the structure determination may be obtained upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, by citing the reference numbers CSD 401725 (for **1**) and 401726 (for **2**), the title and authors of the paper.

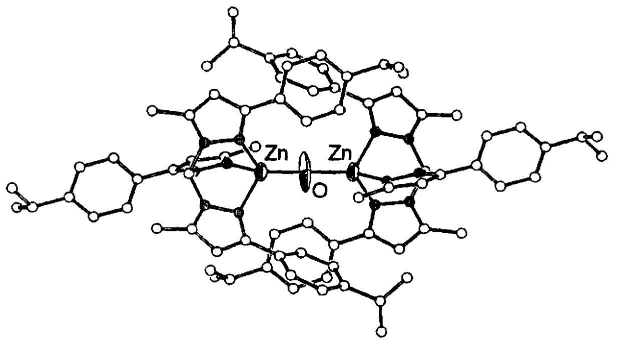


Fig. 1 Molecular structure of compound **1**, drawn with thermal ellipsoids for Zn and O. Selected bond lengths (Å) and angles (°): Zn–N 2.012(8), 2.014(8) and 2.043(8); Zn–O 1.854(1); N–Zn–O 118.0(2), 122.0(2) and 124.8 (2); for Zn–O–Zn see text

ation of the thermal ellipsoid for oxygen indicates a disordered situation with bent Zn–O–Zn linkages. Attempts to refine a disordered model produced Zn–O–Zn angles $\geqslant 172°$ but increased the *R* value by 0.6%. Thus it must be concluded that the Zn–O–Zn angle in **1** is close or identical to 180°, this can also be deduced from the narrow range of Zn–N distances or N–Zn–O angles. The fact that only L′ and not L allows the formation of a $(LZn)_2O$ complex must be related to the close proximity of the two (LZn) units and hence to steric crowding near the centre of the molecule.

While the symmetrical oxide $(LZn)_2O$ was not obtained here, the symmetrical sulfide **2*** seems to have a high tendency to formation. It was obtained from [ZnL(SH)] **3** or [ZnL(SCSOEt)] **4**[9] by heating to 200 °C without a solvent and subsequent crystallization from methanol–benzene. The thermolysis of **3** yielded 87%, that of **4**, which corresponds to a Cugaev elimination with **3** as an intermediate, 83% of **2**.

The molecular structure of compound **2**§ (Fig. 2) represents a compromise resulting from the reluctance of the sulfur atom to adopt a linear arrangement of its two single bonds and the desire of the two L ligands to achieve maximum separation. As a result of this a Zn–S–Zn angle of 139° is observed which is unusually large for singly bonded M–S–M units.[10] The intramolecular steric strain is also obvious from the occurrence of three unusually long Zn–N bonds and two unusually large S–Zn–N angles in the molecule.

Since no other pair of transition-metal complexes $(LM)_2O$ and $(LM)_2S$ with ligands L of the same kind seems to have been reported, the closest analogues for a comparison of the bonding in **1** and **2** are species like $(SiH_3)_2X$[11] or $[(Ph_3PAu)_3X]^+$[12] (X = O or S). Oxygen accepts a larger valence angle than sulfur in all these compounds which according to modern molecular orbital theory can be related to bond polarities and a higher tendency for sp hybridization by oxygen.[13] Accordingly, the electronic nature of **1** and **2** can be described in terms of strongly polar, but covalently bonded Zn–O–Zn and Zn–S–Zn units. The higher polarity allows or favours the linear Zn–O–Zn arrangement in **1** irrespective of the steric requirements of the L ligands, and analogously the bent Zn–S–Zn arrangement in **2** is enforced by electronic reasons despite the steric strain.

The Zn–O and Zn–S bond lengths do not respond to the attachment of two metal atoms to the chalcogen: they are close to those for the simple analogues [ZnL′(OH)] and [ZnL(SH)].[5,9] The fact, however, that **1** is obtained only with L′ while **2** is formed with L can be related to the Zn–X bond lengths: any Zn–O–Zn arrangement (linear or bent) would be impossible for L, but the longer Zn–S bonds give a noticeably longer Zn ··· Zn distance in **2** (4.1 Å) than in **1** (3.7 Å) making it possible to have a bent Zn–S–Zn arrangement even with the bulkier L ligand.

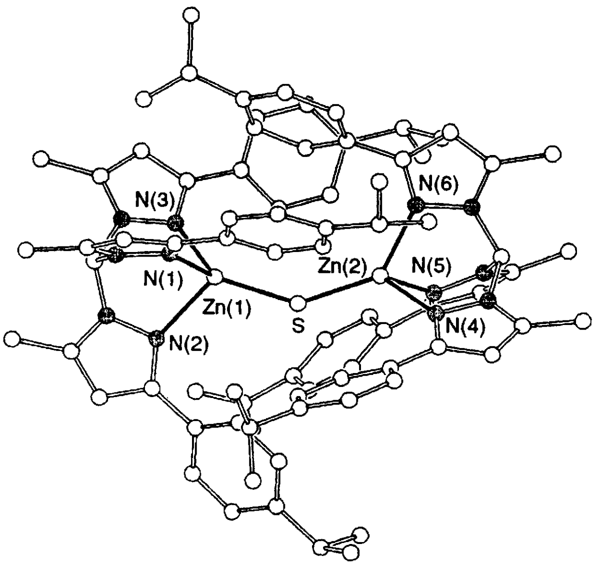


Fig. 2 Molecular structure of compound **2**. Selected bond lengths (Å) and angles (°): Zn(1)–S 2.186(2), Zn(2)–S 2.189(2), Zn(1)–N(1) 2.099(5), Zn(1)–N(2) 2.183(5), Zn(1)–N(3) 2.088(5), Zn(2)–N(4) 2.141(6), Zn(2)–N(5) 2.142(5) and Zn(2)–N(6) 2.066(5); Zn(1)–S–Zn(2) 138.85(10), S–Zn(1)–N(1) 133.5(2), S–Zn(1)–N(2) 112.5(2), S–Zn(1)–N(3) 124.6(2), S–Zn(2)–N(4) 123.8(2), S–Zn(2)–N(5) 111.2(2) and S–Zn(2)–N(6) 136.3(2)

Compounds **1** and **2** provide another demonstration of how the extreme cone angles and inert nature of these substituted pyrazolylborate ligands allow the attachment of unusual coligands to a four-co-ordinated zinc ion. It seems likely that such molecular oxides or sulfides should also exist for other transition metals.

Acknowledgements

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* Compound **4** (200 mg, 0.25 mmol) was heated to 200 °C for 10 min. After washing twice with diethyl ether (10 cm^3) compound **2** (144 mg) remained. ^1H NMR ($CDCl_3$): δ 0.74 (d, 36 H, J^3 6.9), 2.42 (spt, 6 H, J^3 6.9), 2.55 (s, 18 H), 6.20 (s, 6 H), 6.54 (d, 12 H, J^3 8.2) and 7.34 (d, 12 H, J^3 8.2 Hz).

§ See footnote on p. 1915.