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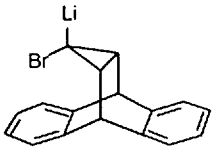
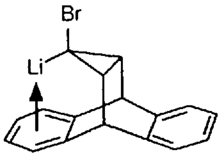


syn-**8**



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Discrimination between S^{2-} and SO^{2-} Sites in Mixed Crystal Compounds Containing Co and Co/Mo Clusters by ^{59}Co-NMR Spectroscopy, and the Relevance for HDS Catalysis

Achim Müller[a]**, Erich Krickemeyer**[a]**, Hartmut Bögge**[a]**, and Dieter Rehder***

Abstract. In aqueous solutions of the mixed crystal compounds with formal composition $K_8[Co_{4-x}Mo_xS_{4-y}(SO)_y(CN)_{12}]\cdot nH_2O$ (x = 0–2; y = 0–2) *i)* there are distinct CoS, Co(SO), and $Co(SO)_2$ sites and *ii)* no hetero-metal clusters are present. These results, revealed by ^{59}Co–NMR, could principally not be disclosed by single crystal X-ray structure analysis. The NMR data also suggest a stable dinuclear cobalt-sulphur cluster in solution. The relevance for HDS catalysis is discussed.

X-Ray diffraction studies of salts with the formal composition $K_8[Co_4S_3(SO)(CN)_{12}]\cdot 4H_2O$ (**I**) [1] and $K_8[Co_{4-x}Mo_xS_2(SO)_2(CN)_{12}]\cdot nH_2O$ (x = 1, n = 6: **II** (*Fig. 1*); x = 2, n = 4: **III**), containing cubane type cluster anions, could only be performed assuming statistical S/SO and/or Co/Mo site occupations in the relevant crystals. As shown in the present study, distinct sites do, however, definitely exist in solution, and these can be unambiguously distinguished by their ^{59}Co–NMR parameters. The use of ^{59}Co–NMR as a sensitive tool in the study of the solution chemistry of diamagnetic Co compounds has been demonstrated earlier [2][3].

The different central units of the cubane-type cluster species **1**, **2**, and **3** (as well as a possible product, **4**) existing in aqueous solutions of **I**, **II**, and **III** are

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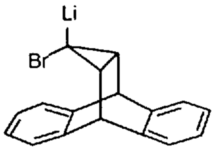

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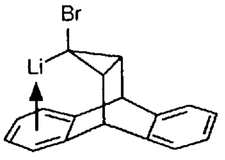

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presented in *Fig. 2*. There are two Co sites in **2**, *viz.* $CoS_3(CN)_3$ (site *a*) and $CoS_2(SO)(CN)_3$ (site *b*) in the ratio of 1:3. Species **3** contains site *b* and $CoS(SO)_2(CN)_3$ (site *c*) in a 1:1 ratio. Selected ^{59}Co–NMR solution spectra of **I**, **II** and **III** are shown in *Fig. 3*. The data are collected in *Table 1*. Chemical shifts $\delta(^{59}Co)$, relative to $[Co(CN)_6]^{3-}$ (δ = 0 ppm), are *ca.* 3300 ppm and, hence, in the expected range for Co^{III} in an octahedral environment of 3 CN and 3 S ligands ($[Co(S_2CNMe_2)_3]$: δ = 6980 ppm [4]). Deshielding of the ^{59}Co nucleus, when cyanide is replaced by an S-functional ligand, is in accord with the less pronounced strength of the latter in a magnetochemical series of ligand strengths [5], and indicative of variations in the ligand-field splitting as the factor dominating shielding.

Trace *A* in *Fig. 3*, obtained for a solution of **I**, corresponds to the mono-oxidized Co cluster **2** (*Fig. 2*) as main component in a mixture which also contains a small amount of the dioxidized cluster **3**. The latter is the main component responsible for the set of spectra represented by traces *B* and *C*, measured for solutions of **II** and **III**, respectively. The low-field resonance is assigned to site *a*, and the high-field resonance to site *c*. The assignment of site *a* is based on the fact that a sharp signal is observed: the point-charge model predicts a vanishing nuclear electric field gradient under C_{3v} symmetry [6] (which is the local symmetry at site *a*) and, hence, minimized quadrupole broadening by the ^{59}Co nucleus ($I = 5/2$, $Q = 0.42 \cdot 10^{-28}$ m^2). The increase of shielding on going from CoS_3 to $CoS_2(SO)$ and further to $CoS(SO)_2$ illustrates that SO^{2-} is a 'stronger' ligand than S^{2-} and/or more easily polarizable.

The spectral pattern in trace *B* (solution of **II**), at ambient temperatures, is dominated by the signal due to *c* (cluster **3**), but **2** is still present. An additional signal due to *d* appears, and the signal due to *b* broadens compared to that in trace *A*. As the temperature rises (*cf.* also *Table 1*), the signal corresponding to *d* increases mainly at the expense of *c*. The temperature effects are reversible. These observations, along with the irregular temperature gradients of $\delta(^{59}Co)$ (*Table 2*), are indicative of a temperature-dependent chemical exchange equilibrium between **2**, **3**, and a third component represented by the resonance due to *d*. A possible candidate causing '*d*' is the binuclear cluster **4** in *Fig. 2*. Since linewidths become smaller with increasing temperature, they are still dominated by the quadrupole relaxation mechanism, and exchange between the various species is slow in the temperature range investigated (285–360 K). Trace *C*, the spectrum exhibited by a solution of the mixed crystal compound $K_8[Mo_2Co_2S_2(SO)_2(CN)_{12}]\cdot 4H_2O$ (**III**), is essentially the same as that of cluster **3**. Hence, there are again individual Co_4 clusters (along with individual Mo_4 clusters) present in solution (see above). It is reasonable to assume that Co clusters according to **1**, **2**, and **3** are also constituents in the mixed crystal compounds **I**, **II** and **III**, and that there are no SO ligands in the Mo_4 cluster, as in the pure, crystalline sample of $K_8[Mo_4S_4(CN)_{12}]\cdot 4H_2O$.

The reason for the promoting effect of Co on MoS_2-based HDS catalysts could not unambiguously be explained until now. We have characterized earlier the 'pseudo-isostructural' metal-sulphur cluster anions $[M_4S_4(CN)_{12}]^{8-}$ (M = Mo, Co) [1][8] (the valence states of the metals in the clusters are comparable to those in the

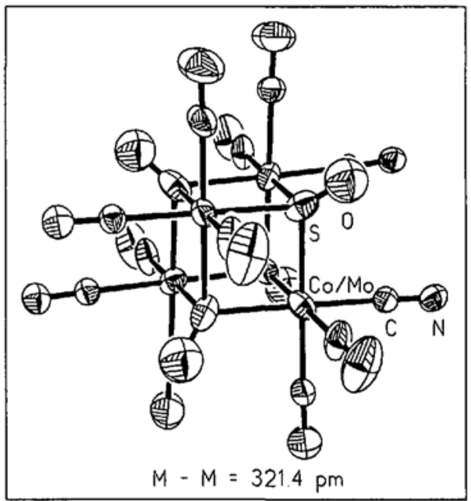

Fig. 1. *Determined 'average' structure of the anions in* **II** (space group $P4_2/nmc$, a = 1230.7(1), c = 1160.4(2) pm; V = 1757.5(4)10^6 pm^3, Z = 2). The best refinement of the structure was observed for a Mo/Co ratio of 1:3 and an S/O ratio of 4:2; R = 0.056, R_w = 0.036. **II** and **III** are isomorphous with $K_8[Co_4S_3(SO)(CN)_{12}]\cdot 4H_2O$ [1].

Table 1. *^{59}Co-NMR Data in D_2O Solution of* **I**, **II**, *and* **III**[a])

Trace[b])	Temp./K	$\delta(^{59}Co)$/ppm (relative intensities (b = 1)) ([$W_{1/2}$[c])/Hz] for the cluster sites)			
		a[d])	*b*[d])	*c*[d])	*d*[d])
A[e])	298	3303 (0.2) [150]	3223 [150]	3179 (0.4) [br]	–
B[f])	285	3283 [sh]	3213 [br]	3164 [2300]	3279 [br]
	298	3305 (1)[190]	3236 [1820]	3181 (2.4)[1550]	3290 (0.5)[br]
	320	3355 (0.8) [190]	3281 [1290]	3233 (1.7) [930]	3340 (0.7)[1260]
	340	3394 (0.8)[150]	3318 [930]	3271 (1.6)[720]	3378 (0.7)[1020]
	360	3435 (0.7)[170]	3357 [780]	3311 (1.4)[510]	341 8 (0.8)[840]
C[g])	298	3304 (1.5)[sh]	3230/3224 [br/sh]	3181 (2.8)[1600]	3288 [br]

[a]) $\delta(^{59}Co)$ values are quoted relative to a saturated solution of $K_3[Co(CN)_6]$ in D_2O.

[b]) See *Fig. 3*.

[c]) Widths of the resonance line at half-height. br. = broad, sh = shoulder.

[d]) *a*, *b*, and *c* correspond to the sites CoS_3, $CoS_2(SO)$, and $CoS(SO)_2$ in the cluster units **1**, **2**, and **3** in *Fig. 2*; and *d* to the Co sites in **4**.

[e]) Solution obtained from **I** (*cf.* **2** in *Fig. 2*).

[f]) Solution obtained from **II** (*cf. Fig. 1* and **3** in *Fig. 2*).

[g]) Solution obtained from **III**.

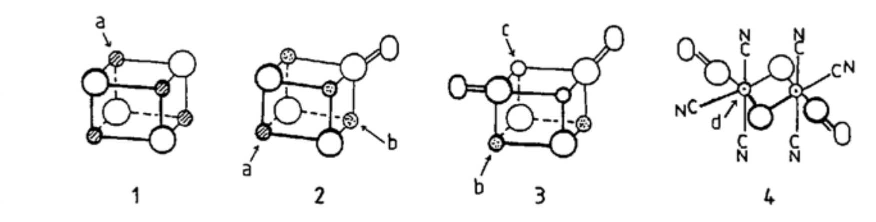

Fig. 2. *Structures of the central units of the cluster species* **1**, **2**, *and* **3**, *together with that of* *$[Co_2S_2(SO)_2(CN)_6]^{8-}$*. Small circles represent $Co(CN)_3$, large circles S sites.

CoMoS phase of the catalyst). Our SCCC-MO calculations [8] have shown that the electron density at the S-atom in the Co cluster is much higher than in the Mo one. Therefore, the Co cluster (but not $[Mo_4S_4(CN)_{12}]^{8-}$) is oxidized in the presence of air ($S^{2-} \rightarrow \mu_3\text{-}SO^{2-}$). One possible influence of Co in the catalyst may arise from the increase of electron density at the S- and Mo-atoms, thus improving activation of H_2, (see also [1b]).

A further result of this investigation is the observation that oxidation of S^{2-} ligands within the Co cluster is more pronounced in the presence of Mo species like those in **II** and **III**.

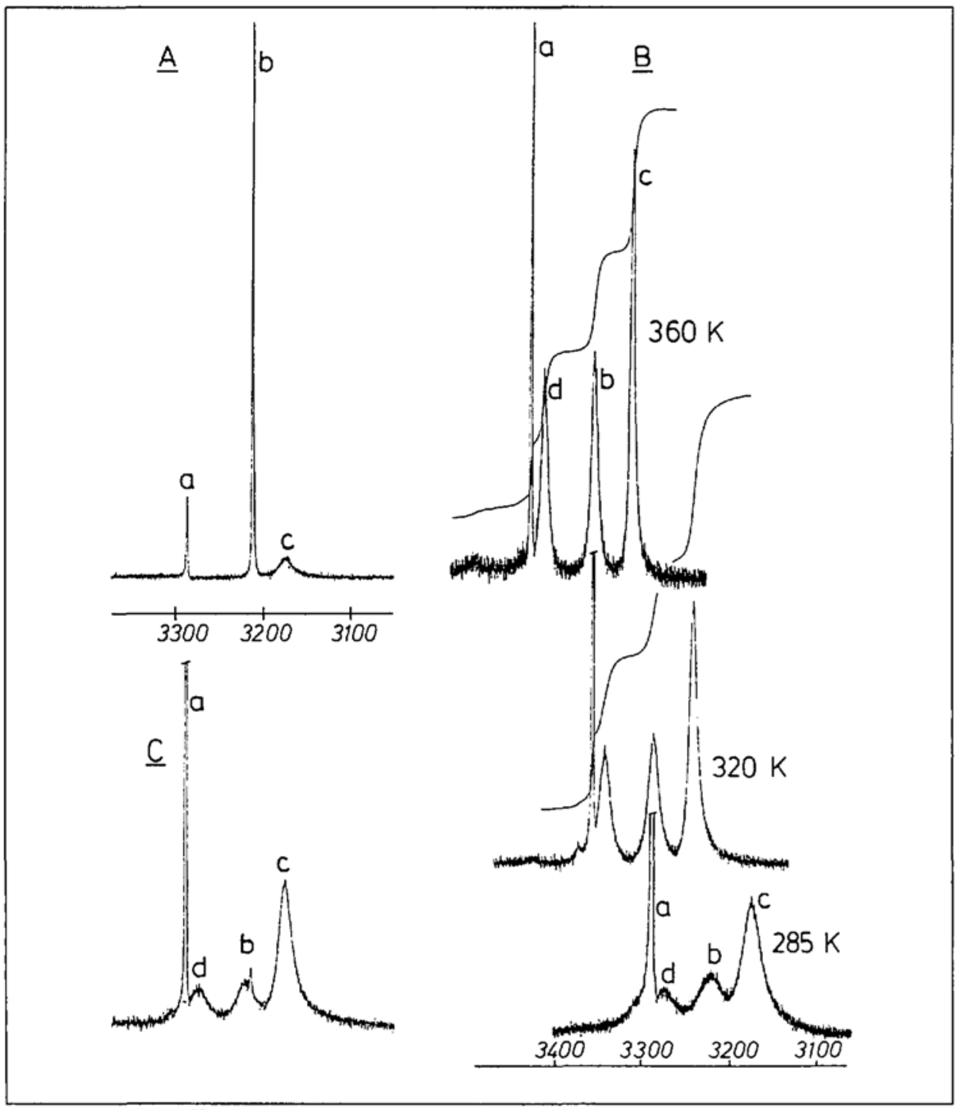

Fig. 3. *85.45 MHz ^{59}Co–NMR spectra of* **I** (*A*), **II** (*B*) and **III** (*C*). The main resonance in trace *A* is due to the cluster **2** (*cf. Fig. 1*), the main species responsible for *B* and *C* is the cluster **3**. *a*, *b*, and *c* correspond to the sites CoS_3, $CoS_2(SO)$, and $CoS(SO)_2$, respectively, *d* is tentatively assigned to the Co sites in the dinuclear cluster **4**.

Table 2. *Temperature Gradients* [ppm/deg] *of the Resonance Signals*[a])

Temperature range	*a*	*b*	*c*	*d*
285–298	1.57	1.64	1.21	0.78
298–320	2.38	2.14	2.48	2.38
320–340	1.95	1.85	1.90	1.90
340–360	2.05	1.95	2.00	2.00

[a]) All resonances shift to low (magnetic) field with an increase in temperature, in accordance with theory [7].

Experimental

^{59}Co NMR spectra were obtained on a *Bruker AM 360* spectrometer at 85.45 MHz in 10-mm diameter vials. Sweep width 83 kHz, 16 K data set, pulse angle 60°, relaxation delay 0.5 s; standard (external): sat. aq. (D_2O) $K_3[Co(CN)_6]$. Samples were dissolved in aq. (deoxygenated D_2O) KCN (*ca.* 0.1 M) solns.

$K_8[Co_4S_3(SO)(CN)_{12}]\cdot 4H_2O$ (**I**) was prepared as described in [1].

$K_8[Co_3MoS_2(SO)_2(CN)_{12}]\cdot 6H_2O$ (**II**): *a*) 1.625 g (6.24 mmol) of freshly prepared $[NH_4]_2[MoS_4]$ was dissolved in 35 ml of H_2O and stirred with 5 ml of conc. aq. HCl. A dark brown precipitate formed, which was filtered off and washed with several portions of H_2O. *b*) 5.25 g (18.68 mmol) of $CoSO_4\cdot 7H_2O$ was dissolved in 55 ml of H_2O and treated with 40 ml of 25% aq. NH_3, immediately followed by passage of H_2S through the soln., again producing a dark brown precipitate, which was washed with several portions of H_2O. *c*) The combined precipitates were suspended in 50 ml of H_2O containing 15 g (0.23 mol) of KCN and heated to 80–90° for 10 min. The greenish brown soln. thus obtained was allowed to stand in a 100 ml *Erlenmeyer* flask (wide-necked, covered with a watch glass) on a hot-plate at 65–70° for 8–10 d. During this time, dark brown crystals of **II** precipitated. These were filtered off the hot soln., and washed with 33% aq. ethanol. From the mother liquor, additional material could be isolated. For single-crystal X-ray data see legend to *Fig. 1*.

$K_8[Co_2Mo_2S_2(SO)_2(CN)_{12}]\cdot 4H_2O$ (**III**): Prepared as described for **II**, but using 12.48 mmol of $[NH_4]_2$ $[MoS_4]$ and 12.45 mmol of $CoSO_4\cdot 7H_2O$. Single-crystal X-ray data for **III**: space group $P4_2/nmc$, $a = 1230.0(2)$, $c = 1157.8(2)$ pm, $V = 1751.6(6)\cdot 10^6$ pm^3, $Z = 2$; refinement for Mo/Co = 2:2, S/O = 4:2; $R = 0.068$, $R_w = 0\,039$.

The accuracy of the determination of the contents of SO-oxygen and water of crystallization in **II** and **III** was limited by disorder problems. An elemental analysis for all elements expected was performed, and confirmed a ratio Mo/Co = 1:3 in **II** and Mo/Co = 2:2 in **III**.

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[1] a) A. Müller, E. Krickemeyer, R. Jostes, H. Bögge, E. Diemann, U. Bergmann, *Z. Naturforsch., B* **1985**, *40*, 1715; b) A. Müller, *Polyhedron* **1986**, *5*, 323.
[2] R.J. Goodfellow, in 'Multinuclear NMR', Ed. J. Mason, Plenum Press, New York 1987, Chapt. 20.
[3] a) D. Rehder, *Magn. Reson. Rev.* **1984**, *9*, 125; b) D. Rehder, in 'Transition Metal Nuclear Magnetic Resonance', Ed. P.S. Pregosin, Elsevier, Amsterdam, 1991, pp. 1–66.
[4] R.L. Martin, A.H. White, *Nature (London)* **1969**, *223*, 394.
[5] J. Mason, *Chem. Rev.* **1987**, *87*, 1299.
[6] J.W. Akitt, W.S. McDonald, *J. Magn. Reson.* **1984**, *58*, 401.
[7] C.J. Jameson, D. Rehder, M. Hoch, *J. Am. Chem. Soc.* **1989**, *109*, 2589.
[8] A. Müller, R. Jostes, W. Eltzner, Chong-Shi Nie, E. Diemann, H. Bögge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogell, Shun Che, S. J. Cyvin, B. N. Cyvin, *Inorg. Chem.* **1985**, *24*, 2872.