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LETTER

An isocyano complex reformulated: the X-ray crystal structure of *trans*-$[Co(CN)(H_2O)(DMGH)_2]$

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As part of our continuing studies on transition-metal cyano complexes [1] we have been investigating cobalt(II) and cobalt(III) dimethylglyoximato complexes ($DMGH_2$, dimethylglyoxime, 2,3-butanedionc dioxime) with cyanide co-ligands as potential antidotes for cyanide poisoning [2], since the related vitamin B12a has such antidotal properties. We were interested therefore in a note in this journal [3] followed by a full paper [4] on the X-ray crystal structures of complexes formulated as $[Co(CN)(H_2O)(DMGH)_2]$ (I) and $[Co(NC)(H_2O)(DMGH)_2]$ (II) (we use here the same numbering system for these complexes as do Solans *et al.* [4]). Since it is generally believed [5, 6] that transition-metal isocyano complexes (i.e. those containing metal–N rather than metal–C bonds) have only a very transient existence, the stability of **II** is surprising, and we have noted anomalies in the vibrational spectra reported for **I** and **II** which did not seem to match with the structures claimed. We decided therefore to reinvestigate the X-ray crystal structure of **II**, and find that while the crystallographic results match those reported for **I**, the spectral data are in agreement with those reported for **II**. The orange material **II** is, therefore, a cyano and not an isocyano complex.

Experimental

Preparation and spectra

The complex formulated [3, 4] as $[Co(NC)(H_2O)(DMGH)_2]$ (**II**) was prepared by the literature method [3] from $[Co(NH_3)_2(DMGH)_2]Cl \cdot 5H_2O$ and $K[Ag(CN)_2]$ and formed orange crystals as reported [3]. *Anal.* Found: C, 32.5; H, 4.8; N, 21.0. Calc. for $C_9CoH_{16}N_5O_5$: C, 32.5; H, 4.8; N, 21.0%. The Raman and infrared spectra of the material gave bands in the $\nu(CN)$ stretching region at 2136 and 2130 cm^{-1}, respectively (compared with Raman and infrared bands at 2136 cm^{-1} reported for **II** [3, 7].

Our attempts to prepare **I** by heating **II** as in the literature [3] gave, instead of the reported brown crystals, a brown non-crystalline material which did however have broad Raman and infrared bands at 2190 and 2180 cm^{-1}, respectively (compared with bands at 2185 and 2186 cm^{-1}, respectively as reported for **I** [3, 7]. We were unable, however, to obtain crystalline samples of this complex suitable for X-ray study.

TABLE 1. Summary of structure of **II**

Complex	$[Co(CN)(H_2O)(DMGH)_2]$	'$[Co(CN)(H_2O)(DMGH)_2]$' (I)	'$[Co(NC)(H_2O)(DMGH)_2$' (II)
Colour	orange	brown	orange
System	monoclinic	monoclinic	monoclinic
a (Å)	10.837(2)	10.867(3)	10.987(3)
b (Å)	9.544(2)	9.581(3)	9.728(3)
c (Å)	7.147(2)	7.156(2)	7.242(2)
β (°)	101.82(2)	101.86(2)	102.08(2)
Volume (Å^3)	723.5^a	729.1	757.0
$\nu(CN)$ (cm^{-1}) R^b	2136	2186	2136
IR^b	2130	2186	2136
Formulated as	cyano complex	cyano complex	isocyano complex
Colour change on heating	orange → brown		orange → brown
Reference	this work	3, 4	3, 4

^{a}At 19 °C. ^{b}R = Raman, IR = infrared data.

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Crystallographic data

The orange crystals of **II** are monoclinic, with $a=10.837(2)$, $b=9.544(2)$ and $c=7.147(2)$ Å, $\beta=101.82(2)°$, $U=723.5$ Å^3 (at 19 °C), space group $P2_1/m$, and $Z=2$. Intensity data were collected on a Nicolet R3m/Eclipse S140 diffractometer system, using graphite-monochromated Cu $K\alpha$ radiation. A total of 971 independent reflections was measured, to $\theta=55°$, of which 209 were judged to be 'unobserved'. Least-squares refinement has now reached $R=0.048$.

Results and discussion

A summary of the X-ray and spectral data from refs. 3 and 4 and of our own redetermination of the structure of **II** is given in Table 1. The unit-cell dimensions of our sample are close to those reported for **I** but not to those reported [4] for **II**. The refinement of the structure is entirely consistent with the orange compound **II** having the formulation $[Co(CN)(DMGH)_2(H_2O)]$, i.e. **II** is a cyano and not an isocyano complex. The most important bond lengths are: Co–C (cyanide), 1.903(8); C–N (cyanide) 1.133(11); Co–O (water) 1.984(7); mean Co–N, 1.889(5) Å.

It is clear that '$[Co(NC)(H_2O)(DMGH)_2]$' (**II**) is simply the expected cyano complex $[Co(CN)(H_2O)(DMGH)_2]$. This conclusion is in keeping with the known coordination chemistry of mixed cobalt(III) dimethylglyoximato–cyano complexes and goes some way to explain the otherwise very puzzling Raman and infrared data reported [3, 7] for **I** and **II**. Raman and infrared bands near 2130 cm^{-1} are exactly where ν(CN) bands for a cobalt(III) cyano complex would be expected to lie [5, 6]. Thus the crystallographic and spectral results are now consistent with each other.

Although we did find, in agreement with Alvarez and Lopez [3], that heating **II** gave a brown material with Raman and infrared bands assignable to ν(CN) near 2180 cm^{-1}, this is the region in which *bridging* cyano ligands are expected to absorb. We note that there is a report of a polymeric brown material $[Co(CN)(DMGH)_2]_n$ which has Raman and infrared bands at 2179 and 2184 cm^{-1}, respectively [7]. We conclude that the orange compound **II** is the cyano complex *trans*-$[Co(CN)(H_2O)(DMGH)_2]$; we do not know what the brown material **I** is but vibrational spectra suggest that it could be a polymeric cyano-bridged species.

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