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Structure and Magnetic Behaviour of Complexes of Chromium with β-Ketoamines

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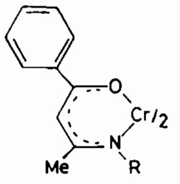
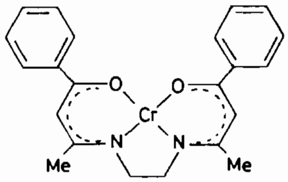


(1)

R = Me, iso-Pr



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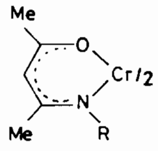
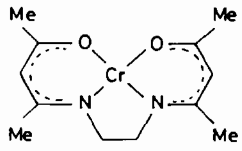


(3)

R = Me, Et, Pr
iso-Pr, Bu



(4)

Cr(acacen)

Numerous complexes are formed by β-ketoamines with bivalent metal ions of the first transition series from manganese(II) to copper(II) [1–3], but the known chromium(II) complexes are restricted to (1) (R = Me, iso-Pr) and (2) which contain bidentate and quadridentate β-ketoamines prepared from benzoylacetone [4]. Detailed structures are lacking, although from its isomorphism with the corresponding palladium(II) complex (1, R = iso-Pr) is believed to be planar [4], and no magnetic measurements have been carried out over a range of temperature.

The new chromium(II) complexes (3) of a series of bidentate β-ketoamines derived from acetylace-

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TABLE I. Magnetic Properties and Selected Bond Distances and Angles.

Complex	μ_{eff} (B.M.)		θ (°)[a]	Complex	Distance (Å)	Angle (°)
	293 K	90 K				
				3, R = Bu		
(3)				Cr–N(1)	2.089	
R = Me	4.26	2.99	126	Cr–N(2)	2.082	
R = Et	4.49	3.16	147	Cr–O(1)	1.964	
				Cr–O(2)	1.962	
R = Pr	4.50	3.83	42	C(1)–C(2), C(7)–C(8)	1.37(av)	
R = iso-Pr	4.69	4.31	24	C(2)–C(3), C(6)–C(7)	1.43(av)	
R = Bu	4.31	3.99	23	O(1)–Cr–N(1)		88.4
				O(2)–Cr–N(2)		89.4
				O(1)–Cr–N(2)		91.0
				N(1)–Cr–O(2)		90.8
				Cr(acacen)		
(4)				Cr–N(1)	2.012	
Cr(acacen)	4.66	3.88	50	Cr–N(2)	2.012	
				Cr–O(1)	1.971	
				Cr–O(2)	1.973	
				C(4)–C(5), C(10)–C(11)	1.42(av)	
				C(5)–C(6), C(9)–C(10)	1.37(av)	
				N(1)–Cr–N(2)		83.0
				O(1)–Cr–O(2)		94.1
				O(1)–Cr–N(1)		91.3
				O(2)–Cr–N(2)		91.5

[a] Curie–Weiss law taken as $\chi_A^{-1} \propto (T + \theta)$.

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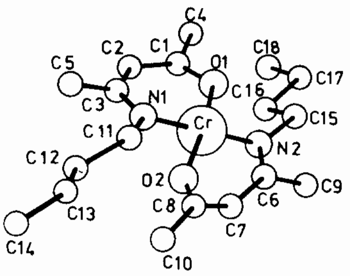

Fig. 1. The molecular structure of complex 3, (R = Bu) $Cr(BuNCMeCHCOMe)_2$.

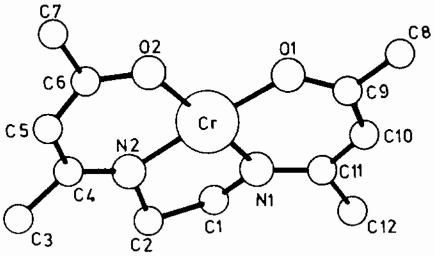

Fig. 2. The molecular structure of Cr(acacen).

tone, and the complex [4,Cr(acacen)] of the quadridentate β-ketoamine N,N'-ethylenebis(acetylacetoneimine)($acacenH_2$), have now been prepared* under nitrogen by a known method [4].

The effective magnetic moments at room temperature are below the value of 4.90 B.M. expected for the high spin $3d^4$ configuration (S = 2) of chromium(II), and decrease still further as the temperature is lowered (Table I). The Weiss constants, θ, of the complexes (3) show an irregular decrease as the bulk of R increases. Complex (4), Cr(acacen), also has a low, temperature-dependent magnetic moment. Such magnetic behaviour is usually considered due to antiferromagnetic interaction, but as there are no obvious pathways for interaction the crystal structures of (3, R = Bu) and Cr(acacen) have been determined.

The molecule of (3, R = Bu) is *trans*-planar (Fig. 1). The similarity of the chelate ring C–C bond distances (Table I) shows that there is considerable π-delocalisation and obligate planarity of each chelate ring. Resemblances between the electronic spectra of series (3) indicate that all are planar.

In Cr(acacen) a *cis* arrangement of the N_2O_2 atoms is imposed by the ligand on the metal ion. The molecule is essentially planar (Fig. 2), and from the bond lengths there is considerable delocalisation in the chelate rings (Table I). The Cr–O bond distances are similar to those in (3, R = Bu), but the Cr–N bond distances are significantly shorter (0.07 Å). This may indicate a greater degree of back bonding since in the *cis* molecule the N atoms do not have to compete for the same metal d_π orbital.

As there are no obvious pathways for antiferromagnetic interaction, it is suggested that the magnetic data can be accounted for by the progressive formation of low spin forms (S = 1 and/or 0) as the temperature is lowered.

Chromium(II) usually forms distorted six coordinate complexes, planar complexes being uncommon, and tetrahedral complexes of simple ligands unknown. Unlike in the nickel(II) series [5] analogous to (3), bulky R groups do not induce the formation of tetrahedral chromium(II); but this work has established a series of planar chromium(II) complexes, the magnetic behaviour of which remains to be explained in detail.

Crystal data: Complex 3, R = Bu^n, crystallises in the orthorhombic system, with a = 9.279(1), b = 13.045(1), c = 33.114(3) Å, V = 4008 $Å^3$, Z = 8, and space group *Pbca*. The intensities of 3100 symmetry-independent reflexions were measured. The structure was determined by the heavy atom method and refined to R = 0.053 for 1823 observed reflexions.

Crystal data: Cr(acacen) crystallises in the monoclinic system, with a = 11.169(1), b = 8.895(1), c = 13.193(1) Å, $\alpha = \gamma = 90°$, $\beta = 95.2°$, V = 1305 $Å^3$, Z = 4, and space group $P2_1/c$. The intensities of 2038 symmetry-independent reflexions were measured. The structure was determined by the heavy atom method and refined to R = 0.045 for 1566 observed reflexions.

The crystal data were measured on an Enraf-Nonius CAD-4 diffractometer (MoKα radiation). The structures were determined by standard Patterson and Fourier methods and refined by full-matrix least squares.

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*Satisfactory microanalyses were obtained.