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COMMUNICATION

REACTION OF NICKEL(II) β-DIKETONATES WITH HYDROXYLAMINE. SYNTHESIS OF NICKEL(II) COMPLEXES OF MONO-OXIMES OF β-DIKETONES (β-KETOOXIMES)

RONALD BENNETT, CHRISTOS BOLOS,* JOHN CHARALAMBOUS† and JASBIR S. LOTA

Department of Applied Chemistry and Life Sciences, The Polytechnic of North London, Holloway Road, London N7 8DB, U.K.

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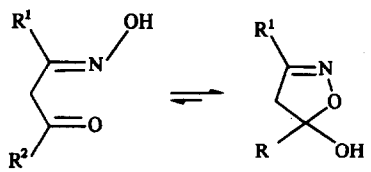
Abstract—Nickel(II) acetylacetonate or benzoylacetonate on treatment with hydroxylamine at 0°C give adducts of the type $Ni(\beta\text{-diket})_2(NH_2OH)_2$ which on heating in refluxing ethanol afford β-ketooximato complexes of the type $Ni(\beta\text{-ketox})_2(H_2O)_2$.

Apart from a report describing briefly the preparation of the nickel(II) and copper(II) bischelates derived from benzoylacetaldehyde mono-oxime (**1**; $R^1 = H$, $R^2 = Ph$)[1] no studies of the synthesis, properties and structure of complexes derived from mono-oximes of β-diketones (**1a**) (henceforth referred to as β-ketooximes and abbreviated as β-ketoxH) have been reported. This contrasts with the very extensive interest shown in complexes derived from related ligands e.g. β-diketones and β-ketoimines.[2] As part of our interest in oximic complexes[3] we have investigated the reaction of hydroxylamine with metal β-diketonates and the potential of this reaction for the synthesis of complexes of β-ketooximes. Here we report briefly on reactions involving nickel(II) β-diketonates and on the successful synthesis of nickel(II) β-ketooximates. The synthesis of complexes of β-ketooximes by the direct reaction of β-ketooximes with metal salts is hindered because β-ketooximes (a) exist entirely or predominantly in the cyclic isoxazoline form (**1b**),[4] and (b) readily dehydrate to give isoxazoles.[5]



(1a) **(1b)**

Reaction of hydroxylamine with a suspension of nickel(II) complexes of acetylacetone and benzoylacetone in ethanol at *ca* 0°C gave hydroxylamine adducts of the type $Ni(\beta\text{-diket})_2(NH_2OH)_2$.

When suspensions of the adducts $Ni(acac)_2(NH_2OH)_2$ and $Ni(bzac)_2(NH_2OH)_2$ in ethanol were heated under reflux, condensation of hydroxylamine with the keto group occurred resulting in the formation of the nickel(II) β-ketooximato chelates $Ni(acacm)_2(H_2O)_2$ (acacmH = 1; $R^1 = R^2 = Me$) and $Ni(bzacm)_2(H_2O)_2$ (bzacmH = 1; $R^1 = Me$, $R^2 = Ph$), respectively.

The formulation of the β-ketooximato chelates is indicated by their elemental analysis and mass spectra which exhibit intense $[Ni(\beta\text{-ketox})_2]^+$ ions. Furthermore, the complex $Ni(bzacm)_2(H_2O)_2$ on treatment with dilute hydrochloric acid afforded *ca* 2 moles of 3-methyl-5-phenylisoxazole per mole of the complex. The nature of the isooxazole indicates

* On leave from the University of Thessaloniki, Greece.

† Author to whom correspondence should be addressed.

Table 1. Yields and analytical data for the new complexes

	Yield (%)	%C	%H	%N	%Ni
$Ni(acac)_2(NH_2OH)_2$	40	37.6 (37.2)	6.5 (6.2)	9.0 (8.7)	18.2 (18.2)
$Ni(bzac)_2(NH_2OH)_2$	75	53.4 (53.5)	5.7 (5.8)	6.2 (6.2)	13.1 (13.1)
$Ni(acacM)_2(H_2O)_2$	50	37.0 (37.2)	6.4 (6.2)	9.0 (8.7)	17.9 (18.2)
$Ni(bzacM)_2(H_2O)_2$	55	53.2 (53.5)	6.1 (5.8)	6.4 (6.2)	12.9 (13.1)

that the condensation occurred at the carbonyl group which is adjacent to the methyl group.

EXPERIMENTAL

Yields, analytical and other data are given in Table 1.

Action of hydroxylamine on Ni(β-diket)$_2$

Hydroxylamine (25 mmol) and Ni(β-diket)$_2$ (10 mmol) were stirred in anhydrous ethanol at 0°C. After 24 h Ni(β-diket)$_2$(NH$_2$OH)$_2$ was filtered off, washed with ethanol and dried *in vacuo*.

Preparation of Ni(β-ketox)$_2$(H$_2$O)$_2$

A suspension of Ni(β-diket)$_2$(NH$_2$OH)$_2$ (5 mmol) in anhydrous ethanol (50 cm^3) was heated under reflux for 8 h. Filtration gave Ni(β-ketox)$_2$(H$_2$O)$_2$ which was washed with ethanol and dried *in vacuo*. Hydroxylamine (25 mmol) and Ni(β-diket)$_2$ (10 mmol) were stirred in anhydrous ethanol at 0°C. After 24 h Ni(β-diket)$_2$(NH$_2$OH)$_2$ was filtered off, washed with ethanol and dried *in vacuo*.

Acidolysis of Ni(bzacm)$_2$(H$_2$O)$_2$

Ni(bzacm)$_2$(H$_2$O)$_2$ (1.0 g, 2.2 mmol) was stirred with hydrochloric acid (15%, 10 cm^3) for 1 h. The resulting mixture was diluted with water, neutralized and extracted with diethyl ether. After drying the extract ($MgSO_4$), removal of the diethyl ether gave 3-methyl-5-phenyl-isoxazole (0.5 g, 85%), m.p. 65–67°C (ref. 6, 67°C). (Found: C, 75.5; H, 5.8; N, 8.8. Calc. for $C_{10}H_9NO$: C, 75.7; H, 5.7; N, 8.8%); *m/z* 159 (M^+).

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