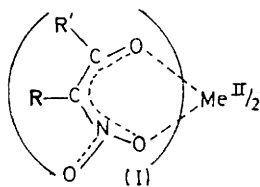


## Complexing Properties of $\alpha$ -Nitroketones. Part II.<sup>1,2</sup> Complexes of 2-Nitroacetophenone and Nitroacetone with Chromium(III), Iron(III), and Aluminium(III)

By Rosalba Astolfi, Ines Collamati, and Claudio Ercolani,\* C.N.R. Laboratory, Istituto di Chimica Generale ed Inorganica, Università di Roma, Roma, Italy

Neutral complexes of 2-nitroacetophenone (napH) and nitroacetone (naH),  $[ML_3]$  ( $M = Cr^{III}, Fe^{III},$  and  $Al^{III}$ ), have been isolated. Visible spectra of the  $Cr^{III}$  species and  $X$ -ray powder measurements establish a six-co-ordinate structure for all the complexes, as indicated by the stoichiometry and bidentate  $O$ -donor behaviour of the  $\alpha$ -nitro-ketonic group. Two crystalline forms of the complex tris(2-nitroacetophenonato)chromium(III) have been obtained. These are probably *cis-trans*-isomers arising from the unsymmetrical nature of the chelating ligands. Only one form could be obtained for the other  $ML_3$  species described, and all have been tentatively assigned a *trans*-structure.

In a previous paper<sup>2</sup> our systematic investigation of the complexing properties of  $\alpha$ -nitroketones, previously started with 2-nitroacetophenone ( $PhCOCH_2NO_2, napH$ ), was extended to several other ligands of the same class of compounds. Without exception, in all



complexes  $[ML_2]$  and  $[ML_2B_n]$  ( $M = Co^{II}$  or  $Ni^{II}$ ;  $B =$  solvent molecule;  $n = 2$  or  $3$ ) the  $\alpha$ -nitroketonato-

<sup>1</sup> Presented in part at the 13th Internat. Conf. Co-ordination Chem., Zakopane, Poland, 14th–22nd September, 1970.

anion (L) was shown to co-ordinate to the metal ion (M) as a bidentate chelating agent [as in (I)], whatever the nature of the substituents attached to the chelating moiety. By using  $Cr^{III}$ ,  $Fe^{III}$ , and  $Al^{III}$  metal ions, and napH and nitroacetone ( $MeCOCH_2NO_2, naH$ ) as ligands, neutral complexes  $[ML_3]$  were also isolated and they are reported in the present paper. Attempts to isolate similar complexes of  $Mn^{II}$ ,  $Co^{III}$ , and  $Rh^{III}$  were unsuccessful.

### EXPERIMENTAL

2-Nitroacetophenone (napH) and nitroacetone (naH) were prepared as previously described.<sup>2,3</sup>

(2-Nitroacetophenonato)thallium(I),  $[Tl(nap)]$ .—A warm

<sup>2</sup> D. Attanasio, I. Collamati, and C. Ercolani, *J.C.S. Dalton*, 1972, 772 and references therein.

<sup>3</sup> C. Ercolani, I. Collamati, and G. Sartori, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1966, **40**, 558.

solution of 2-nitroacetophenone (330 mg, 0.002 mol) in ethanol was added to a solution of the complex  $\text{Tl}(\text{OCO-Me})$  (530 mg, 0.002 mol) in the same solvent at 50 °C. Yellow crystals of the  $[\text{Tl}(\text{nap})]$  complex were immediately formed; after cooling, these were filtered off, washed with ethanol, and dried (quantitative yield). The complex is stable and may be kept in air indefinitely. It is insoluble in water and the usual organic solvents, but slightly soluble in dimethylformamide.

*(Nitroacetato)thallium(I)*,  $[\text{Tl}(\text{na})]$ .—This complex was prepared in quantitative yield by a method similar to that used for  $[\text{Tl}(\text{nap})]$ , by reacting equimolar amounts of  $[\text{Tl}(\text{OCOMe})]$  and nitroacetone in warm ethanol. Pale yellow crystals were obtained, which were recrystallized from water. The complex is unstable in air and must be kept at 0 °C in the dark. It darkens on heating at 100 °C and melts at ca. 140 °C.

*Tris(2-nitroacetophenonato)chromium(III)*,  $[\text{Cr}(\text{nap})_3]$ .—A solution of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (133 mg, 0.0005 mol) in dimethylformamide (5 cm<sup>3</sup>) was added dropwise over ca. 20 min, with stirring, to a suspension of the complex  $[\text{Tl}(\text{nap})]$  (645 mg, 0.00175 mol) in the same solvent (30 cm<sup>3</sup>). After another 30 min,  $\text{TiCl}$  was filtered off, and the solution evaporated under vacuum at room temperature. The brown solid so obtained was first washed with cold benzene. On cooling and evaporating in air, brown crystals of  $[\text{Cr}(\text{nap})_3]$  were obtained. These were always contaminated by the presence of very small amounts of a yellow crystalline material which, on the basis of elemental analysis, must also be given the formula  $[\text{Cr}(\text{nap})_3]$  [(b) in Table I]. Because of the lower solubility and of the tendency of the yellow form (b) to isomerize in hot benzene, the separation of pure crystals of the brown form of the complex  $[\text{Cr}(\text{nap})_3]$  could be accomplished by repeated crystallizations from that solvent (yield 40%).

*Tris(nitroacetato)chromium(III)*,  $[\text{Cr}(\text{na})_3]$ .—A warm solution (50 °C) of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  (150 mg, 0.000565 mol) in dimethylformamide (5 cm<sup>3</sup>) was added dropwise with stirring, over ca. 20 min, to a warm solution of the complex  $[\text{Tl}(\text{na})]$  (612 mg, 0.002 mol) in the same solvent (25 cm<sup>3</sup>). After another 30 min, the warm solution was set aside to cool. The  $\text{TiCl}$  which formed was filtered off and the solution was evaporated under vacuum at room temperature. The reddish brown solid residue was dissolved in cold benzene and the solution was slowly evaporated in air. Brown crystals of the complex  $[\text{Cr}(\text{na})_3]$ , impure of tar-like products, were formed. These were combined with those obtained from other preparations, redissolved in benzene, and the solution concentrated by evaporation in air. This was repeated until the tar-like products were completely removed and an analytically pure product obtained. The complex prepared in this way contains one molecule of benzene, which is slowly lost on exposure to air or on heating at 80 °C ( $10^{-2}$  mmHg).

*Tris(2-nitroacetophenonato)aluminium(III)*,  $[\text{Al}(\text{nap})_3]$ .—2-Nitroacetophenone (716 mg, 0.00434 mol) was added in one step to a solution of  $\text{AlCl}_3$  (166 mg, 0.00124 mol) in anhydrous benzene under  $\text{N}_2$ , with stirring, at a temperature of ca. 40 °C. The reaction continued with the evolution of  $\text{HCl}$  for ca. 2 h. After a further 40 min, the solid product was filtered off, washed with anhydrous benzene, and then dried *in vacuo*. Alternatively  $[\text{Al}(\text{nap})_3]$  could be obtained, in high yield, by the reaction of  $[\text{Al}(\text{isopropoxide})_3]$  with 2-nitroacetophenone (molar ratio 1:3.5) in anhydrous benzene.

*Tris(nitroacetato)aluminium(III)*,  $[\text{Al}(\text{na})_3]$ .—Nitroacetone (447 mg, 0.00434 mol) was added to a solution of  $\text{AlCl}_3$  (166 mg, 0.00124 mol) in anhydrous benzene (30 cm<sup>3</sup>), with stirring, under a slow stream of  $\text{N}_2$ , at a temperature of 40 °C. The reaction was allowed to continue until no more hydrogen chloride was evolved, and then for a further 60 min. Anhydrous hexane was then added to the solution to precipitate the complex which was filtered off and dried *in vacuo*.

*Tris(2-nitroacetophenonato)iron(III)*,  $[\text{Fe}(\text{nap})_3]$ .—The complex  $[\text{Tl}(\text{nap})]$  (1.67 g, 0.00455 mol) was added to a suspension of sublimed  $\text{FeCl}_3$  (213 mg, 0.0013 mol) in warm (40 °C) anhydrous benzene (40 cm<sup>3</sup>), with stirring under a stream of  $\text{N}_2$ . A strong reddish brown colour was immediately produced. The reaction was stopped after ca. 2.5 h. The  $\text{TiCl}$  formed and excess of  $[\text{Tl}(\text{nap})]$  were separated by decanting the solution, under  $\text{N}_2$ , into another vessel. The benzene solution was brought to dryness. The solid brown residue was washed once or twice, with a small amount of anhydrous benzene, then several times with hot anhydrous heptane, and dried *in vacuo*.

*Tris(nitroacetato)iron(III)*,  $[\text{Fe}(\text{na})_3]$ .—For the preparation of this complex a method similar to that used for  $[\text{Fe}(\text{nap})_3]$  was applied. The reaction between  $\text{FeCl}_3$  and  $[\text{Tl}(\text{na})]$  (molar ratio 1:3.5), in anhydrous benzene at room temperature, was allowed to proceed for ca. 2 h, with stirring. The benzene solution was set aside, then separated from the  $\text{TiCl}$  and excess of  $[\text{Tl}(\text{na})]$ , and finally evaporated to dryness at reduced pressure giving a solid residue of pure  $[\text{Fe}(\text{na})_3]$ .

*Physical Measurements*.—Reflectance and solution spectra, magnetic measurements, and X-ray powder patterns were obtained as previously.<sup>2</sup> I.r. spectra of KBr pellets in the region 4000—400 cm<sup>-1</sup> were run on a Beckman IR-9 instrument at both room and liquid-nitrogen temperatures.

## RESULTS AND DISCUSSION

The complexes of formulae  $[\text{ML}]$  and  $[\text{ML}_3]$  are given in Table I, together with some of their properties. Two crystalline forms of  $[\text{Cr}(\text{nap})_3]$  [(a) and (b)] have been isolated. The well established behaviour of the  $\alpha$ -nitroketonato-group as a bidentate O-donor<sup>2</sup> and the stoichiometry of the  $[\text{ML}_3]$  complexes allow these latter to be straightforwardly assigned a six-co-ordinate tris(chelate) structure, as supported also by their visible and i.r. spectra (see below).

The brown form (a) of the complex  $[\text{Cr}(\text{nap})_3]$ , obtained as well shaped prismatic crystals, was repeatedly examined by X-ray crystallography, but always failed to provide a clear, readable, powder pattern. The X-ray powder spectrum of the yellow form (b) (Table 2) unequivocally establishes its isomorphism with the complex  $[\text{Fe}(\text{nap})_3]$ . The powder spectrum of the complex  $[\text{Al}(\text{nap})_3]$  is less easily interpretable, because of the presence of additional diffraction lines (nos. 6, 12, 18, and 20) which are not present in the spectra of the  $\text{Cr}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$  analogues. All three complexes of nitroacetone had identical X-ray powder spectra and thus constitute an isomorphous series.

Forms (a) and (b) of the complex  $[\text{Cr}(\text{nap})_3]$  show identical electronic and vibrational spectra. The electronic reflectance and solution spectra in chloroform indicate, as expected, an octahedral or quasi-octahedral symmetry, in that they show, below 20.0 kK, only one absorption with a maximum at 17.4 kK ( $\epsilon$  98 l mol<sup>-1</sup> cm<sup>-1</sup>), which, in  $O_h$  symmetry, can be assigned to the transition

of  $[\text{Cr}(\text{nap})_3]$ . This can be explained on the basis of the opposite inductive effects produced by the groups attached to the chelating ring, if identical geometrical features of the ring are assumed in the two complexes. Again, high-intensity absorptions above 20.0 kK in the spectrum of  $[\text{Cr}(\text{na})_3]$  prevent the location of the other two expected spin-allowed  $d-d$  absorptions.

TABLE 1  
Some properties and elemental analyses (%) of  $[\text{ML}]$  and  $[\text{ML}_3]$  complexes

Complex	Colour	M.p. (t/°C)	Calc.			Found		
			C	H	N	C	H	N
$[\text{Ti}(\text{nap})]$	Yellow	183	26.05	1.65		26.5	1.9	
$[\text{Ti}(\text{na})]$	Yellow	140	11.75	1.3		11.95	1.05	
$[\text{Cr}(\text{nap})_3]$ (a) *	Brown	160 †	52.95	3.3	7.7	53.4	3.45	7.8
(b)	Yellow		52.95	3.3	7.7	53.0	3.55	7.2
$[\text{Cr}(\text{na})_3]$ , C <sub>6</sub> H <sub>6</sub>	Brown		41.3	4.15	9.65	40.9	4.2	9.4
$[\text{Cr}(\text{na})_3]$ *	Brown	200 †	30.15	3.35	11.75	30.2	3.6	11.0
$[\text{Al}(\text{nap})_3]$	White	202	55.5	3.45	8.1	54.8	3.8	8.25
$[\text{Al}(\text{na})_3]$	White	145 †	32.45	3.6	12.6	31.8	3.5	12.3
$[\text{Fe}(\text{nap})_3]$	Red-brown	150 †	52.55	3.3	7.65	52.8	3.45	7.3
$[\text{Fe}(\text{na})_3]$	Red-brown	100 †	30.0	3.3	11.6	30.3	3.4	11.3

nap = 2-Nitroacetophenonato and na = nitroacetonato.

\* Room-temperature magnetic moments,  $\mu_{\text{eff}}$ : 3.86 B.M. for  $[\text{Cr}(\text{nap})_3]$  and 3.89 B.M. for  $[\text{Cr}(\text{na})_3]$ . † With decomposition. ‡ Slight decomposition starts at 126–128 °C.

TABLE 2  
X-Ray powder spectra of  $[\text{ML}_3]$  complexes

No.	$[\text{Cr}(\text{nap})_3]$		$[\text{Fe}(\text{nap})_3]$		$[\text{Al}(\text{nap})_3]$		$[\text{Cr}(\text{na})_3]$		$[\text{Fe}(\text{na})_3]^a$		$[\text{Al}(\text{na})_3]$	
	<i>I</i>	<i>d</i> <sub>exp</sub>	<i>I</i>	<i>d</i> <sub>exp</sub>	<i>I</i>	<i>d</i> <sub>exp</sub>	<i>I</i>	<i>d</i> <sub>exp</sub>	<i>I</i>	<i>d</i> <sub>exp</sub>	<i>I</i>	<i>d</i> <sub>exp</sub>
1	s <sup>b</sup>	13.70	m	14.37	s	14.25	vs	7.58	s	7.51	vs	7.60
2			s	12.81	s	12.63	s	6.42	m	6.42	s	6.38
3	m	8.80	m	9.16	m	8.93	vs	6.07	s	6.11	vs	6.09
4			w	7.90	w	7.73					w	5.89
5	vw	5.63	vw	5.98	vw	5.81	w	5.58	vw	5.61	w	5.56
6			s	5.34	w	5.08						
7	vw	5.07	m <sup>b</sup>	5.10	m	5.07	s	4.74	m	4.69	m	4.76
8			w	4.68	s	4.73	w	4.20	vw	4.18	vw	4.18
9	w <sup>b</sup>	4.37			w	4.41	m	4.05	m	4.05	s	4.03
10					w	4.16	s	3.64			s	3.63
11	s	3.83	s	3.84	s <sup>b</sup>	3.87	vs	3.53	s	3.57	vs	3.52
12					m	3.54	m	3.36	w	3.36	m	3.33
13	w <sup>b</sup>	3.28			m	3.31	w	3.18	vw	3.17	w	3.19
14					vw	3.23	m	3.05			m	3.05
15	vw	3.03	m	3.14	m	3.15	w	2.91			w	2.90
16	vw	2.71			vw	2.82	vw	2.78			w	2.80
17	vs	2.71	vs	2.72							w	2.61
18					vw	2.42	vw	2.56			w	2.53
19	w	2.21	w	2.22			vw	2.41			vw	2.40
20					w	2.00	vw	2.33			vw	2.31
21	w	1.92	w	1.92	w	1.95	vw	2.25			vw	2.24
22	w	1.71	w	1.72			vw	2.17			vw	2.17
23	m	1.57	m	1.57			vw	2.06			vw	2.05
24	vw	1.35	vw	1.36							vw	1.99
25	vw	1.28	vw	1.28							vw	1.95
26	vw	1.21	vw	1.21			vw	1.89			vw	1.89
27											vw	1.83
28											vw	1.80
29							vw	1.77			vw	1.76

nap = 2-Nitroacetophenonato and na = nitroacetonato.

<sup>a</sup> Film of weak intensity. <sup>b</sup> Diffuse band.

${}^4A_{2g} \rightarrow {}^4T_{2g} (\equiv \Delta)$ . At higher frequencies absorptions of high intensity in the spectra of both forms mask the other two expected spin-allowed bands. For the complex  $[\text{Cr}(\text{na})_3]$  the lowest energy  $d-d$  absorption is found, both for the solid and in chloroform solution, at a frequency (17.8 kK,  $\epsilon$  71 l mol<sup>-1</sup> cm<sup>-1</sup>) slightly higher than the corresponding absorption found in the spectrum

of  $[\text{Cr}(\text{nap})_3]$ . The energy of the  ${}^4A_{2g} \rightarrow {}^4T_{2g}$  transition ( $\equiv \Delta$ ) for the complexes  $[\text{Cr}(\text{nap})_3]$  and  $[\text{Cr}(\text{na})_3]$  very closely approaches that of similar  $\beta$ -diketonate complexes of chromium(III), e.g. tris(benzoylacetonato)chromium(III) ( $\Delta$  17.75 kK),<sup>4</sup> tris(acetylacetonato)chromium(III) ( $\Delta$

<sup>4</sup> R. C. Fay and T. S. Piper, *J. Amer. Chem. Soc.*, 1962, **84**, 2303.

17.85 kK),<sup>5</sup> and a series of other complexes.<sup>6</sup> These data indicate that the  $\alpha$ -nitroketonic and  $\beta$ -diketonic groups occupy very close positions in the spectrochemical series. A similar, although more approximate, indication was obtained from a comparison of the spectra of the  $[\text{NiL}_2]$  and  $[\text{NiL}_2(\text{py})_2]$  species<sup>2</sup> (py = pyridine) with those of the analogous  $\beta$ -diketonate complexes of nickel(II).<sup>7</sup>

I.r. spectra of form (b) of  $[\text{Cr}(\text{nap})_3]$  and of the complexes  $[\text{Fe}(\text{nap})_3]$  and  $[\text{Al}(\text{nap})_3]$  were taken at room and liquid-nitrogen temperatures, but no significant differences were observed as a function of temperature. Absorptions related to internal vibrations of the  $\alpha$ -nitroketonic group are given in Table 3 for the region 1 600—

TABLE 3

Wavenumbers ( $\text{cm}^{-1}$ ) and assignments of chelating-ring vibrations of the complexes  $[\text{M}(\text{nap})_3]$  in the region 1 600—1 200  $\text{cm}^{-1}$

$\text{Cr}(\text{nap})_3$	$\text{Fe}(\text{nap})_3$	$\text{Al}(\text{nap})_3$	Assignment
1 520	1 516	1 540	$\nu(\text{C}=\text{O})$
1 465	1 466	1 473	$\nu(\text{C}=\text{C})$
1 411	1 407	1 425	$\nu(\text{N}=\text{O})$
1 260	1 268	1 295	$\nu(\text{N}=\text{O})$
1 235	1 260	1 274	$\nu(\text{C}=\text{N})$

nap = 2-Nitroacetophenonato.

1 200  $\text{cm}^{-1}$ . The assignments have been made on the basis of the more detailed i.r. study carried out by M. Maltese on the complex  $\text{Cu}(\text{nap})_2$ .<sup>8</sup> It can be seen from Table 3 that the positions of all the absorptions, including  $\nu(\text{C}=\text{O})$  and  $\nu(\text{N}=\text{O})$ , are significantly affected by the change of the metal ion, thus confirming that both groups are directly pointing towards the central metal ion.

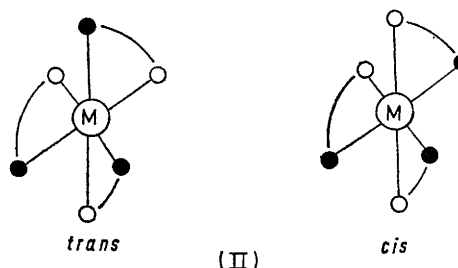
Because of the tris(chelate) nature of the  $[\text{ML}_3]$  species and the non-equivalent co-ordination sites of the

<sup>5</sup> D. W. Barnum, *J. Inorg. Nuclear Chem.*, 1961, **21**, 221.

<sup>6</sup> R. L. Lintvedt and L. K. Kernitsky, *Inorg. Chem.*, 1970, **9**, 491 and references therein.

<sup>7</sup> D. P. Graddon, *Co-ordination Chem. Rev.*, 1969, **4**, 1.

$\alpha$ -nitroketonic group, two geometrical isomers [*cis* and *trans*, or *fac* and *mer*, (II)] are possible for these species. This kind of isomerism has, in fact, been observed in several  $[\text{ML}_3]$  species obtained from unsymmetrical  $\beta$ -diketones and the absolute structure has been established for most of these complexes by using n.m.r. spectra.<sup>4,9</sup> It seems reasonable to think of the two forms (a) and (b) of the complex  $[\text{Cr}(\text{nap})_3]$  as a case of *cis-trans*-isomerism. However, they could not be



examined by n.m.r. because of their paramagnetism, as was also the case for the complex  $[\text{Fe}(\text{nap})_3]$ . The complex  $[\text{Al}(\text{nap})_3]$  is diamagnetic and therefore suitable in this respect for n.m.r. studies; however, it is only slightly soluble in organic solvents and its solutions are unstable. Thus n.m.r. techniques could not be used to determine absolute configuration. Similar difficulties were encountered and precluded n.m.r. investigation on all the  $[\text{M}(\text{na})_3]$  species. Since a *trans*-configuration is in general more probable and has been more frequently observed for the series of  $\text{M}^{\text{III}}$   $\beta$ -diketonate complexes,<sup>4,9</sup> we also suggest a *trans*-arrangement for the two series of isomorphous  $\alpha$ -nitroketonate complexes reported here.

[2/1808 Received, 31st July, 1972]

<sup>8</sup> M. Maltese, personal communication.

<sup>9</sup> R. C. Fay and T. S. Piper, *J. Amer. Chem. Soc.*, 1963, **85**, 500; R. A. Palmer, R. C. Fay, and T. S. Piper, *Inorg. Chem.*, 1964, **3**, 875; R. J. York, W. D. Bonds, jun., B. P. Cotsoradis, and R. D. Archer, *ibid.*, 1969, **8**, 789 and references therein.