

CHEMICAL AND SPECTROSCOPIC STUDIES IN METAL β -DIKETONATES

III.* NITRATION OF METAL BENZOYLACETONATES AND DIBENZOYLMETHANATES

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The results of our study on halogenation¹ and nitration² reactions of quasi-aromatic metal acetylacetonates and on thiocyanation of metal 1,3-diketonates³ under electrophilic substitution reaction conditions have been reported recently. The present article describes some interesting observations and results recorded during the course of nitration of five benzoylacetones and dibenzoylmethanates of aluminium(III), chromium(III), cobalt(III), and palladium(II), and their infrared and electronic spectral studies.

Experimental

Tris(2-nitro-1-phenyl-1,3-butanedionato)aluminium(III), tris(2-nitro-1-phenyl-1,3-butanedionato)chromium(III), tris(2-nitro-1-phenyl-1,3-butanedionato)cobalt(III), tris(2-nitro-1,3-diphenyl-1,3-propanedionato)cobalt(III), and bis(2-nitro-1-phenyl-1,3-butanedionato)palladium(II) have been prepared for the first time by one or both of the procedures (1) and (2) reported by us earlier.²

Cr bzac₃, Co bzac₃, Pd dbm₃, and Co dbm₃ (bzac = benzoylacetone, dbm = dibenzoylmethanate) were prepared as described in the literature.^{4,5} Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. The infrared spectra of all the new nitro derivatives of metal 1,3-diketonates have been recorded on a Perkin-Elmer 137B Infracord (4000–670 cm⁻¹ region) in Nujol mulls or with KBr pellets. Electronic spectra were obtained using a Cary 14 recording spectrophotometer in chloroform.

Results and Discussion

The properties and analytical data of nitro derivatives of metal β -diketonates are listed in Table I. Although successive replacement of methyl groups in metal acetylacetonates by phenyl groups tends to increase the electron density at the central carbon atom of the chelate ring due to small contributions from various resonance forms,⁶ the attack at this carbon atom by the nitronium ion becomes

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¹ Singh, P. R., and Sahai, R., *Aust. J. Chem.*, 1967, **20**, 639.

² Singh, P. R., and Sahai, R., *Aust. J. Chem.*, 1967, **20**, 649.

³ Singh, P. R., and Sahai, R., *Inorg. chim. Acta*, 1968, **2**, 102.

⁴ Collman, J. P., Moss, R. A., Maltz, H., and Heindel, C. C., *J. Am. chem. Soc.*, 1961, **83**, 531.

⁵ Bauer, H. F., and Drinkard, W. C., *J. Am. chem. Soc.*, 1960, **82**, 5031.

⁶ Nakamoto, K., Morimoto, Y., and Martell, A. E., *J. phys. Chem.*, 1962, **66**, 346.

increasingly difficult. This difficulty in attack by the nitronium ion, apparently due to the increased steric hindrance by the phenyl rings which are more or less coplanar with the chelate ring, is evident from the decreased yield of the nitro chelates and increased reaction time (6 hr for metal acetylacetonates,² 6–8 hr for metal benzoylacetonates, and 8–10 hr for metal dibenzoylmethanates). A characteristic feature of the nitration reactions is that whereas the nitration at the central carbon atom of the chelate ring is successfully carried out by $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in acetic anhydride medium (a possible mechanism has been proposed²), dehydrated $\text{Cu}(\text{NO}_3)_2$ fails to react under the same conditions. A similar observation has also been made by Collman.⁷ In the existing literature, no reason appears to have been advanced for this difference; however, we think that while $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ produces Cu^{2+} and NO_3^- ions in acetic anhydride solution to form the acetyl nitrate desired for nitration via a nitronium ion, dehydrated $\text{Cu}(\text{NO}_3)_2$, having predominantly covalent bonding in the molecule,^{8,9} does not produce a sufficient concentration of acetyl nitrate in the nitrating mixture.

TABLE I
NITRATED METAL β -DIKETONATES

Compound	M.P.	Yield (%)		Found (%)				Calc. (%)			
		by (1)	by (2)	C	H	N	M	C	H	N	M
$\text{Al}(\text{C}_{10}\text{H}_8\text{NO}_4)_3$	215–216 ^a	50	—	55.1	4.0	6.3	4.3	55.8	3.7	6.5	4.2
$\text{Cr}(\text{C}_{10}\text{H}_8\text{NO}_4)_3$	245–246 ^b	62	60	54.4	3.4	6.6	7.9	53.7	3.6	6.3	7.8
$\text{Co}(\text{C}_{10}\text{H}_8\text{NO}_4)_3$	165 ^c	54	55	53.3	3.7	6.0	8.8	53.2	3.5	6.2	8.7
$\text{Co}(\text{C}_{15}\text{H}_{10}\text{NO}_4)_3$	155–157 ^c	48	45	62.0	3.4	4.5	6.8	62.6	3.5	4.9	6.8
$\text{Pd}(\text{C}_{10}\text{H}_8\text{NO}_4)_3$	195–196 ^d	—	50	46.5	3.2	5.1	20.3	46.3	3.1	5.4	20.5

^a Yellow needles from benzene. ^b Brown needles from benzene–heptane. ^c Dark green crystals from chloroform–ethanol. ^d Melts with decomposition; yellow needles from chloroform.

An interesting observation in this study has been the oxidation of cobalt(II) to cobalt(III) under nitration reaction conditions of procedure (2).² A reaction time of 6 hr that was necessary for the conversion of cobalt(II) into cobalt(III) does not seem to favour the idea of air oxidation which requires vigorous bubbling of air for several hours through solutions of cobalt(II) to be oxidized, in presence of the ligand. It is conceivable that NO_3^- is responsible for the observed oxidation in our experiments. It is noteworthy in this connection that Livingstone¹⁰ has recently reported NO_2^- and CN^- as being able to oxidize cobalt(II) to cobalt(III).

The principal i.r. absorption bands common to all chelates and their possible assignments in most cases are recorded in Table 2. Our assignments of infrared absorption bands are based on the recent findings by Behnke and Kakamoto¹¹ which have also necessitated revision of some of the assignments made by us previously.² Serious overlapping of the absorption bands due to the phenyl ring

⁷ Collman, J. P., Marshall, R. L., Young, W. L. (III), and Goldby, S. D., *Inorg. Chem.*, 1962, **1**, 704.

⁸ Wallwork, S. G., *Proc. chem. Soc.*, 1959, 311.

⁹ Addison, C. C., and Logan, N., *Preparative inorg. React.*, 1964, **1**, 141.

¹⁰ Ho, R. K. Y., Livingstone, S. E., and Lockyer, T. N., *Aust. J. Chem.*, 1966, **19**, 1179.

¹¹ Behnke, G. T., and Nakamoto, K., *Inorg. Chem.*, 1967, **6**, 433, 440.

with those of the chelate rings makes the assignments difficult. The spectra of $\text{Al}(\text{NO}_2\text{-dbm})_3$ and $\text{Cr}(\text{NO}_2\text{-dbm})_3$, in which some of the absorption bands were incorrectly identified earlier,² have been re-examined and the results included in the same table.

TABLE 2

INFRARED ABSORPTION FREQUENCIES (cm^{-1})

Possible assignments: 1, $\text{C}=\text{O}$ str; 2, asym NO_2 str; 3, $\text{C}=\text{C}$ str; 4, CH_3 deg def; 5, uncertain; 6, sym NO_2 str; 7, $\text{C}=\text{C}$ str + $\text{C}-\text{R}$ str; 8, CH_3 rock; 9, $\text{C}-\text{R}$ str + other modes; 10, $\text{C}-\text{Ph}$ antisym str; 11, uncertain; 12, $\text{C}-\text{N}$ vib or $\text{N}-\text{O}$ vib; 13, $\text{M}-\text{O}$ str + ring def + $\text{C}-\text{R}$ str

Compound	1	2	3	4	5	6	7	8	9	10	11	12	13
$\text{Al}(\text{C}_{10}\text{H}_8\text{NO}_4)_3$	1550s	1517s	1452s	1410sh	1350s	1336s	1300w	1005sh	—	—	875s	820s	685m
$\text{Al}(\text{C}_{18}\text{H}_{10}\text{NO}_4)_3$	1550s	1530s	1450s	—	—	1348s	1300w	—	950m	930w	—	825s	685m
$\text{Cr}(\text{C}_{10}\text{H}_8\text{NO}_4)_3$	1540s	1521s	1450s	1410w	1350s	1345s	1300w	1025w	—	—	870s	822s	685m
$\text{Cr}(\text{C}_{18}\text{H}_{10}\text{NO}_4)_3$	1540s	1525s	1450s	—	—	1350s	1315m	—	980w	930w	—	825s	685m
$\text{Co}(\text{C}_{10}\text{H}_8\text{NO}_4)_3$	1540s	1510s	1450s	1410sh	1350m	1340s	1300w	1020w	—	—	875s	822s	688m
$\text{Co}(\text{C}_{18}\text{H}_{10}\text{NO}_4)_3$	1540s	1510s	1440s	—	—	1343s	1300w	—	980w	930w	—	825s	690m
$\text{Pd}(\text{C}_{10}\text{H}_8\text{NO}_4)_3$	1550s	1524s	1448s	1410w	1348s	1338s	1300w	1020w	—	—	875s	822s	685m

We observed slow development of a deep red colour of solutions of $\text{Al}(\text{NO}_2\text{-acac})_3$, $\text{Al}(\text{NO}_2\text{-bzac})_3$, and $\text{Al}(\text{NO}_2\text{-dbm})_3$ in pyridine, on keeping. This is due to the charge-transfer complex formation between pyridine (donor) and nitrated chelate (acceptor). The λ_{max} (charge-transfer) band has been observed at $\simeq 490 \text{ m}\mu$ in each case. A detailed report on such charge-transfer complexes will be published elsewhere.

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