Synthesis and Biological Activity of Some New β-Diketone Complexes of Cr(III)

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Various substituted β -diketone complexes of Cr(III) have been synthesised and characterised on the basis of analytical, infrared, nuclear magnetic resonance, electronic spectral and magnetic susceptibility data. The antimicrobial study of the complex was made against S. aureus and E. coli. Most of them have exhibited moderate antibacterial activity. A probable correlation of activity and the structure has been established.

INTRODUCTION

The wide profile of biological activities such as bactericidal¹, fungicidal², germicidal^{3,4} and anticancer⁵ have been shown by chalcones. Some methoxy and hydroxy β -diketones are of pharmaceutical⁶ important compounds. Some naphthyl and phenanthryl β -diketones exhibit potent bactericidal and carcinogenic activity⁷. The o-hydroxy β -diketones are good chelating agents used for determination of metal ions⁸⁻¹¹. In the present paper the co-ordination behaviour of some new various substituted β -diketone Cr(III) complexes is reported and structure activity relationship has been established.

EXPERIMENTAL

All the chemicals used were of reagent grade quality. The ligands diaroyl methanes were synthesised by Baker Venkataraman transformation 12,13 of o-hydroxy acetophenones. The substituted acrylophenones were prepared by condensation of various substituted aromatic aldehyde in the presence of base 14 .

Preparation of Cr(III) Metal Complexes

Aqueous solution of chromium chloride and ethanolic solution of substituted acrylophenones were mixed in the 1:3 molar ratio and dilute solution of ammonium hydroxide was added till yellowish brown coloured complexes precipitate out (pH>4.5). The complexes were filtered, washed with distilled water, ethanol and dried. The microanalytical data of Cr(III) complexes have been presented in Table 1.

RESULTS AND DISCUSSION

The elemental analyses indicate that the metal to ligand ratio of 1:3 for chromium(III) complexes. All the complexes are non-hygroscopic,

TABLE 1
PHYSICAL, ANALYTICAL AND MAGNETIC MOMENT DATA OF CHROMIUM(III) COMPLEXES

R ₃ R ₄ R ₄ X ₄ Y ₄ Y ₅ Y ₆ Y ₆ Y ₆ Y ₇	Compound				Groups	ě.	ć	I	M.pt. Decomp.	Anal	Analysis % Found (Calcd)	(Calcd)	uerr
NO, CH, H NO, CH, H NO, CH, CH, CH, CH, CH, CH, CH, CH, CH, CH	punoduno	R3	Rs	R6	x,		Ys		temp.	Z	ס	Č	B.M.
H CH; H H H 304 308 794 H H H H H H 306 2.96 770 H H H H H H H 179 H H H H H H 179 300 3.10 8.07 H CH; H H H H H H 173 H CH; H	[C69H30O24N6Cr]Cl3	NO.	CH3	H	NO	Н	НО	н	270	5.53	7.04	3.04	2.74
H H CH, NO, OH H H H 300 2.96 7.70 NO, CH, H H H CI 2.96 7.70 7.73 H CH, H H CI 260 5.69 7.70 H CH, H H CI H 300 3.10 8.00 H CH, H H CH H H H H H NO, CH, H H	[C ₆₉ H ₄₈ O ₁₅ N ₃ Cr1C] ₃	Н	CH3	H	NO	Н	Н	Ή	304	3.08	7.94	3.83	t
H H CH3 NO3 H H H CH3 NO3 H								:	-	(3.19)	(8.07)	(3.94)	3.70
NO. CH. H H CI 660 7.23 H CH. H NO. H CI H 300 3.10 8.00 H CH. H H H H H H 300 3.10 8.00 H CH. H H H H H H 300 3.10 8.00 H CH. H H H H H H H H 300 2.79 7.45 H CH. H H H OCH. 300 2.79 7.45 H CH. H H CH. H H CH. H H H CH. H H CH.	[C69H48O18N3Cr]Cl3	H	H	CH;	NO NO	НО	н	Н	300	2.96	7.70	3.70	3.75
H CH; H NO; H CI H 300 (3.10) (8.09) H CH; H H H H H 10H 310 (3.19) (8.09) H CH; H H H OH H 165 (3.19) (8.09) H CH; H NO; H OCH; CCH; CCH; CCH; CCH; CCH; CCH;	[C69H42O21N6Cr]Cl3	NO3	CH_3	Н	NO.	Н	Н	ರ	260	5.69	7.23	3.48	;
H CH ₃ H NO ₂ H Cl H 300 3.10 8.00 H CH ₃ H H H H H H H 310 - 8.90 H CH ₃ H NO ₂ H CH H H H H H 60.00 H CH ₃ H NO ₂ H H OCH ₃ 225 5.33 6.78 H CH ₃ H NO ₂ H H OCH ₃ OCH ₃ 300 2.79 H CH ₃ H H H H CH ₄ H C ₂ H ₃ 135 - 8.33 H CH ₃ H NO ₂ H H NOCH ₃ OCH ₃ 250 5.02 H CH ₃ H NO ₂ H H NOCH ₃ OCH ₃ 135 - 8.33 H CH ₃ H NO ₂ H H NOCH ₃ OCH ₃ 250 5.02 H CH ₃ H NO ₂ H H NOCH ₃ 250 5.02 H CH ₃ H NO ₂ H H NOCH ₃ 250 5.02 H CH ₃ H NO ₂ H NOCH ₃ NOCH ₃ 300 5.69 H CH ₃ H NO ₂ H NOCH ₃ H NOCH ₃ 285 2.69 CH CH ₃ H NO ₂ H NOCH ₃ H NOCH ₃ 285 2.69 CH CH ₃ H NO ₂ H NOCH ₃ H OCH ₃ 285 2.69 CH CH ₃ H NO ₂ H NOCH ₃ H OCH ₃ 285 2.69 CH CH ₃ H NO ₂ H NOCH ₃ H OCH ₃ 285 2.69 CH CH ₃ H NO ₂ H NOCH ₃ H OCH ₃ 285 2.69 CH CH ₃ H NO ₂ H NO ₂ H NOCH ₃ 285 2.69 CH CH ₃ H NO ₂ H NO ₂ H OCH ₃ 285 2.69 CH CH ₃ H NO ₂ H NO ₂ H OCH ₃ 285 2.69 CH CH ₃ H NO ₂ H NO ₂ H OCH ₃ NOCH ₃ 285 CH CH ₃ H NO ₂ H NO ₂ H OCH ₃ NOCH ₃ 285 CH CH ₃ H NO ₂ CH ₃ H NO ₂ H OCH ₃ 285 CH CH ₃ H NO ₂ CH ₃ H NO ₂ CH ₃ H OCH ₃ 285 CH CH ₃ H NO ₂ CH ₃ H NO ₂ CH ₃ H OCH ₃ 285 CH CH ₃ H NO ₂ CH ₃ H NO ₂ CH ₃ H OCH ₃ 285 CH CH ₃ H NO ₂ CH ₃ H NO ₂ CH ₃ H OCH ₃ 285 CH CH ₃ H NO ₂ CH ₃ H NO ₂ CH ₃ H OCH ₃ 285 CH CH ₃ H NO ₂ CH ₃ H NO ₂ CH ₃ H OCH ₃ 285 CH CH ₃ H NO ₂ CH ₃ H NO ₂ CH ₃ H NO ₂ CH ₃										(5.79)	(7.34)	(3.59)	3.73
H CH ₃ H H H H H H H H H H H S10 — 8.90 H CH ₃ H H H H OCH ₄ 165 — 8.54 NO ₂ CH ₃ H NO ₂ H H OCH ₃ 225 5.33 6.78 H CH ₃ H NO ₂ H H OCH ₃ OCH ₃ 300 2.79 7.45 H CH ₃ H H H CH ₃ H C ₂ H ₃ 135 — 8.33 H CH ₃ CH ₃ H H H C ₂ H ₃ 135 — 8.33 H CH ₃ CH ₃ H NO ₂ H CH ₃ OCH ₃ 250 5.02 6.40 CH ₃ CH ₃ H NO ₂ H H NCH ₃ 300 5.69 7.23 H CH ₃ H NO ₂ CH ₃ H OCH ₃ R S20 5.69 CH ₃ CH ₃ H NO ₂ H H NCH ₃ 300 5.69 6.97 CH ₃ CH ₃ H NO ₂ H OCH ₃ R S20 6.69 CH ₃ CH ₃ H NO ₂ H NO ₂ H NCH ₃ 285 2.69 6.97 CH ₃ CH ₃ H NO ₂ CH ₃ H OCH ₃ R CH ₃ R CH ₃ C	[C69H45O15N3Cr]Cl3	Ħ	CH3	Ħ	NO.	H	ರ	H	300	3.10 (3.19)	8.00 (8.09)	3.85 (3.95)	3.78
H CH ₃ H H H OH H 165 — (9.00) NO ₂ CH ₃ H NO ₂ H H OCH ₃ CCH ₃ 225 5.33 6.78 H CH ₃ H NO ₂ H H OCH ₃ OCH ₃ 225 (5.44) (6.90) H CH ₃ H H H OCH ₃ OH 295 — (8.06) H CH ₃ H H H H C ₂ H 135 — (8.44) NO ₄ CH ₃ H NO ₂ H CH ₃ OCH ₃ 250 5.02 6.40 H CH ₃ NO ₂ H H NOCH ₃ 250 5.02 6.40 CH ₃ CH ₃ H NO ₂ H OCH ₃ CCH ₃ 285 2.69 6.97 CH ₃ CH ₃ H NO ₂ CCH ₃ H OCH ₃ 285 2.69 6.97 CH ₃ CH ₃ H NO ₂ CCH ₃ H OCH ₃ 285 2.69 6.97 CH ₃ CH ₃ H NO ₂ CCH ₃ H OCH ₃ CRH ₃	[C,9H5,O,Cr]Cl3	Н	CH_3	H	Н	H	Н	H	310	. 1	8.90	4.29	
H CH ₃ H H H H OCH ₄ 165 — 8.54 NO ₂ CH ₃ H NO ₂ H H OCH ₄ 225 5.33 6.78 H CH ₃ H NO ₂ H H OCH ₄ 300 2.79 7.45 H CH ₃ H H H OCH ₄ OCH ₅ SP — 8.33 H CH ₃ H H H CH ₄ H C ₂ H ₃ SP — 8.33 NO ₂ CH ₃ H H H H C ₂ H ₃ SP — 8.33 H CH ₃ CH ₃ H NO ₂ H OCH ₄ SCH ₃ SP — 8.33 H CH ₄ CH ₅ H NO ₂ H H NCH ₄) ₂ 300 5.62 H CH ₅ H NO ₂ CH ₃ H OCH ₅ CH ₅ SP — 6.40 (5.14) (5.51) H CH ₅ H NO ₂ OCH ₅ H OCH ₅ SP 2.69 (5.18) (7.35)										I	(00.6)	(4.40)	3.80
NO ₂ CH ₃ H NO ₂ H H OCH ₄ 225 5.33 6.78 (5.90) (5.44) (6.90) (6.9	[C69H51O12Cr]Cl3	H	CH_3	Н	н	Н	НО	н	165	!	8.54	4.12	
H CH ₃ H NO ₂ H H OCH ₃ 225 5.33 6.78 (5.44) (6.90) (6.90) H CH ₃ H NO ₂ H H OCH ₃ OH 2.79 7.45 (7.56) H CH ₃ H H H H C ₂ H ₃ 135 - (8.06) H CH ₃ H NO ₂ H OCH ₃ OCH ₃ 250 5.02 H CH ₃ H NO ₂ H OCH ₃ OCH ₃ 250 5.02 H CH ₃ H NO ₂ H OCH ₃ NOCH ₃ 280 5.03 H CH ₃ NO ₂ H H OCH ₃ NOCH ₃ 280 5.69 (5.14) (6.51) H CH ₃ H NO ₂ OCH ₃ H OCH ₃ 285 2.69 (7.10)										ı	(8.65)	(4.22)	3.75
H CH ₃ H NO ₂ H H OCH ₃ 300 2.79 7.45 (2.98) (7.56) H CH ₃ H H H OCH ₃ OH 295 - (8.06) H CH ₃ H H H C ₂ H ₃ 135 - (8.36) NO ₂ CH ₃ H NO ₂ H OCH ₃ OCH ₃ 250 5.02 6.40 (5.14) (6.51) H CH ₃ NO ₂ OCH ₃ H OCH ₃ 285 2.69 6.97 (7.35)	[C12H51O24N6Cr]Cl3	NO2	CH_3	H	NO2	Н	Н	OCH3	225	5.33	6.78	3.27	
H CH ₃ H NO ₂ H H OCH ₃ 300 2.79 7.45 (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.56) (2.98) (7.10)				ł						(5.44)	(6.90)	(3.37)	3.81
H CH H H H COCH ₃ OH 295 — 7.95 H CH ₃ H H H H C ₂ H ₃ 135 — 8.33 NO ₂ CH ₃ H NO ₂ H OCH ₃ OCH ₃ 250 5.02 6.40 H H CH ₃ NO ₂ H H N(CH ₃) ₂ 300 5.69 (5.14) CH CH ₃ H NO ₂ OCH ₃ H OCH ₃ 285 2.69 6.97 (7.35)	[C11H54O18N5Cr]Cl3	H	CH3	H	NO2	Н	H	0CH3	300	2.79 (2.98)	7.45 (7.56)	3.60 (3.69)	3.85
H CH ₃ H H H H C ₂ H ₃ 135 – (8.06) NO ₂ CH ₃ H NO ₂ H OCH ₃ OCH ₃ 250 5.02 6.40 H H CH ₃ NO ₂ H H N(CH ₃) ₂ 300 5.69 7.23 H CH ₃ H NO ₂ OCH ₃ H OCH ₃ 285 2.69 6.97 (2.80) (7.10)	[C ₂₁ H ₅ ,O ₁₅ Cr]Cl ₃	H	CH	Н	Н	Н	OCH3	НО	295	, ,	7.95	3.85	
H CH ₃ H H H H C ₂ H ₃ 135 – 8.33 NO ₂ CH ₃ H NO ₂ H OCH ₃ OCH ₃ 250 5.02 6.40 (5.14) (6.51) H CH ₃ NO ₂ H H N(CH ₃) ₂ 300 5.69 7.23 H CH ₃ H NO ₂ OCH ₃ H OCH ₄ 285 2.69 6.97 (7.35)										I	(8.06)	(3.94)	3.72
- (8.44) - NO ₂ CH ₃ H NO ₂ H OCH ₃ OCH ₃ 250 5.02 6.40 (5.14) (6.51) - H H CH ₃ NO ₂ H H N(CH ₃) ₂ 300 5.69 7.23 H CH ₃ H NO ₂ OCH ₃ H OCH ₄ 285 2.69 6.97 (2.80) (7.10)	[C ₁₅ H ₅₁ O ₅ Cr]Cl ₅	H	CH,	H	Н	Ή	н	C_2H_3	135	ı	8.33	4.00	
H NO ₂ CH ₃ H NO ₂ H OCH ₃ OCH ₃ 250 5.02 6.40 (5.14) (6.51) H H CH ₃ NO ₂ H H N(CH ₃) ₂ 300 5.69 7.23 H CH ₃ H NO ₂ OCH ₃ H OCH ₄ 285 2.69 6.97 (2.80) (7.10)										ı	(8.44)	(4.12)	3.83
(5.14) (6.51) (6.51) (7.23) (7.35) (7.35) (7.35) (7.35) (7.35)	[C,3H,3,O,1,N,Cr]Cl,	NO2	CH3	H	NO.	H	OCH3	OCH;	250	5.02	6.40	3.09	6
H H CH, NO, H H N(CH,), 300 5.69 7.23 (5.81) (7.35) H CH, H NO, OCH, H OCH, 285 2.69 6.97 (2.80) (7.10)										(5.14)	(6.51)	(3.18)	3.80
(3.81) (7.35) H CH, H NO, OCH, H OCH, 285 2.69 6.97 (2.80) (7.10)	[C ₇₅ H ₆₅ O ₁₅ N ₆ Cr]Cl ₃	H	H	CH_3	NO	H	H	N(CH3)2	300	5.69	7.23	3.48	t
H CH; H NO; OCH; H OCH; 285 2.69 6.97 (2.80) (7.10)										(5.81)	(7.35)	(3.59)	3.77
(7.10)	[C,5H60O21N3Cr]Cl3	H	CH;	H	NO.	OCH3	Н	OCH,	285	2.69	6.97	3.36	ć
										(7.80)	(7.10)	(3.47)	3.79

insoluble in water and many of the common organic solvents. Magnetic moment of the Cr(III) complexes have been found to lie in the range 3.70–3.85 B.M. (Table 1) indicating the presence of three unpaired electron supporting octahedral geometry of complexes.

Due to intramolecular hydrogen bonding in o-hydroxy aromatic aldehydes and ketones ν C—OH generally observed at 3410 cm⁻¹. This band was found to be absent in IR spectra of Cr(III) complexes. The co-ordination of the oxygen of the hydroxyl group is confirmed by the lowering of ν C—O from 1100–1120 to 1040–1060 cm⁻¹. Two sharp and strong bands assigned for ν C—O at 1680, 1600 cm⁻¹ in the free ligand, the band at lower frequency region is lowered by 50–60 cm⁻¹ on complexation thereby indicating the co-ordination from carbonyl oxygen. All the complexes showed a band at 450 cm⁻¹ to ν (Cr—O). The ν (C—O) (phenolic) is observed in the free ligand at 1280 cm⁻¹ and on complexation with transition metals this band shift to higher energy by about 40–55 cm⁻¹ indicating phenolic oxygen co-ordination of the acrylophenone.

The bands have been observed for the Cr(III) complexes, at 20833 and 26315 cm⁻¹. These may be assigned to the $A_{2g} \rightarrow T_{2g}$ and $A_{2g} \rightarrow T_{1g}$ transitions respectively.

In the 1H nmr spectra, the signals due to aromatic —CH₃ observed as singlet at δ , 2.3 while the aromatic protons are encountered as the multiplet between δ , 6.8–7.5 ppm. The nmr signal due to —OH (phenolic) group was found to be disappeared because of the complexation with the metal atom.

All the complexes were screened for their antimicrobial activity by agar diffusion technique¹⁶ using dimethyl formamide solvent against Staphylococcus aureus (gram + ve) and Escherichia coli (gram - ve) bacteria at 25 to 50 μ g/ml concentration. The tetracycline was used as standard compound for comparison. These complexes were found to be moderately active against gram + ve and gram - ve bacteria. The presence of halogen as well as nitro group in the ligand moiety of the complexes enhances the bacteristatic activity.

REFERENCES

- 1. P. F. Diveti, A. Timoney and M. A. Vickars, J. Org. Chem., 26, 4941 (1961).
- 2. N. P. Buu-hoi and N. D. Xuong, J. Org. Chem., 23, 39 (1958).
- 3. S. S. Misra and R. S. Tewari, Indian J. Appl. Chem., 35, 95 (1972).
- 4. S. S. Mishra, J. Indian Chem. Soc., 50, 68 (1973).
- 5. S. C. Kushawaha Dinakar and J. B. Lal, Indian J. Chem., 5, 82 (1967).
- 6. C. W. Wilson and D. E. Iloyo, J. Pharmacol. Exp. Ther., 95, 399 (1949).
- 7. M. Kamoda, J. Agri. Chem. Soc., Jpn., 28, 791 (1954).

- 8. K. Syamasundar, Proc. Indian Acad. Sci., 60, 259 (1964).
- 9. K. Syamasundar, Proc. Indian Acad. Sci., 60, 259 (1964).
- 10. R. R. Naidu, Curr. Sci. (India), 37, 342 (1968).
- 11. R. R. Naidu, Talanta, 22, 615 (1975).
- 12. W. Baker, J. Chem. Soc., 1381 (1933).
- 13. K. Venkataraman and H. S. Mahal, Curr. Sci. (India), 2, 214 (1933).
- M. B. Hogale, B. N. Pawar, A. R. Shelar and B. P. Nikam, Oriental J. Chem., 3, 57 (1987).
- 15. L. J. Bellamy, The IR Spectra of Complex Molecules, Methuen, London, p. 95 (1976).
- 16. M. M. Nandi and A. K. Misra, Trans. Bose Res. Inst., 19, 44 (1981).

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