367. *The* $C\equiv N$ *Stretching Frequency in Metal Complexes of 3-Cyanopentane-2,4-dione.*

By John P. Fackler, jun.

The preparation of 3-cyanopentane-2,4-dione is described. The infrared stretching frequencies of the $C\equiv N$ group in twelve metal complexes of this β-diketone are recorded. While marked variations in the position of the $C\equiv N$ stretching frequency are found with changes in the co-ordination number of the metal ion, the position of the band is found at 2216·2 ± 1·0 cm.$^{-1}$ in six tervalent complexes. It appears that the $2p_\pi$-electrons of the chelate ring are not strongly perturbed by interaction with the $3d$-orbitals of the metal.

Some degree of " benzenoid " resonance (I; M = metal) has been suggested to help account for the unusual stability of metal acetylacetonates.[1] Unfortunately some authors have used this concept indiscriminately, especially in an effort to explain the ultraviolet spectra of these complexes.[2] Holm and Cotton [3] discuss the plausibility of " benzenoid " resonance in view of the charge separations demanded by this model. They suggest that " although extensive $O_{p\pi} \longrightarrow M_{p\pi}$ (or $d\pi$) bonding does not appear likely, some mixing of the $O_{p\pi}$ and metal $p\pi$ and/or $d\pi$ orbitals will doubtless occur." This mixing undoubtedly affects the electronic spectra [3] of the complexes. However, since electronic spectra reflect perturbations of excited as well as ground electronic states of the ligand by the

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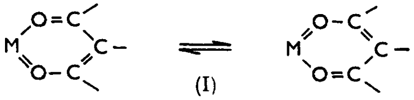
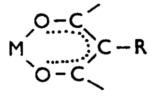
[1] Calvin and Wilson, *J. Amer. Chem. Soc.*, 1945, **67**, 2003.

[2] Basy and Chatterji, *Z. phys. Chem.* (*Liepzig*), 1958, **209**, 360.

[3] Holm and Cotton, *J. Amer. Chem. Soc.*, 1958, **80**, 5658.

metal ion, one must unravel the relative effect of these perturbations on both empty and filled π-orbitals of the ligand before a satisfactory interpretation of the spectra can be presented.


(I)


(II)

The electron spin resonance spectrum[4] of $Cu(acac)_2$ (acac = acetylacetonyl) has been interpreted as suggesting weak metal–oxygen σ-bonding but fairly strong metal–oxygen π-bonding in this complex. Spin density distribution studies[5] on $V(acac)_3$ have indicated appreciable unpaired electron density on the –CH and $-CH_3$ groups. Apparently some degree of $O_{p\pi}$–$M_{d\pi}$ mixing occurs in the ground state of these complexes. In a recent paper by Nakamoto *et al.*,[6] it was concluded from infrared spectroscopic measurements that the metal–oxygen bonds in β-diketone complexes of cobalt(III), chromium(III), and aluminium(III) are strong while in the iron(III) complex they are weak. These authors also suggested that "resonance involving *dπ–pπ* bonding does not occur in the Al(III) [β-diketone] complexes."

The "quasiaromatic" character of the ring (II) is sufficient to account for the reactivity of the methylene carbon atom to electrophilic substitution.[7] This also satisfies available structural data which generally suggest equivalent sets of M–O, C–O, and C–C bonds in $Cu(acac)_2$,[8] $VO(acac)_2$,[9] $Fe(acac)_3$,[10] $Al(acac)_3$,[10] $Cr(acac)_3$,[11] $Co(acac)_3$,[11] and $Be(acac)_3$.[12]

During an extensive investigation of β-diketone complexes[13] of copper(II), designed to characterize thoroughly the electronic absorption bands of the chelate ring, bis-(3-cyanopentane-2,4-dione)copper(II) was prepared. This complex showed a strong C≡N stretching frequency at ~2212 cm.$^{-1}$. The position of this band appeared to be significantly shifted from the position of most C≡N stretches.[14] Since the cyano-group is conjugated to the chelate ring in metal complexes of this ketone, the frequency and intensity of the infrared band might give some indication concerning the extent of the interaction between the metal ion and the ligand π-system.

The Table lists the frequencies and intensities observed for 3-cyanopentane-2,4-dione and twelve of its metal complexes. The stretching frequencies listed are generally 10—20 cm.$^{-1}$ lower than those observed for cyano-groups in aromatic nitriles[14] (aliphatic, 2240—2260; aromatic, 2221—2240; conjugated aliphatic, 2218—2232 cm.$^{-1}$). With *para*-substituted benzonitriles, there is a progressive shift toward lower frequencies in the order,[14-16] $NO_2 > CN > Me,Cl > NH_2$, which corresponds to increasing electron density on the carbon atom attached to the cyano-group. Several authors have suggested that intensities of C≡N bands also increase as the electron density on the carbon attached to the cyano-group increases.[6,17]

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[4] McGarvey, *J. Phys. Chem.*, 1958, **60**, 71; Maki and McGarvey, *J. Chem. Phys.*, 1958, **29**, 31, 35; Kivelson and Neiman, *J. Chem. Phys.*, 1961, **35**, 149.

[5] Forman, Murrell, and Orgel, *J. Chem. Phys.*, 1959, **31**, 1129.

[6] Nakamoto, McCarthy, Ruby, and Martell, *J. Amer. Chem. Soc.*, 1961, **83**, 1066.

[7] Djordjevic, Lewis, and Nyholm, *Chem. and Ind.*, 1959, 122; Collman, Moss, Goldby, and Trahanovsky, *ibid.*, 1960, 1213; Khuiber, *J. Amer. Chem. Soc.*, 1960, **82**, 4839; Collman and Kittleman, *ibid.*, 1961, **83**, 3529.

[8] Shugam, *Doklady Akad. Nauk S.S.S.R.*, 1951, **81**, 853.

[9] Dodge, Templeton, and Zalkin, *J. Chem. Phys.*, 1961, **35**, 55.

[10] Roof, Jr., *Acta Cryst.*, 1956, **9**, 781.

[11] Shugam and Shkolnikova, *Doklady Akad. Nauk S.S.S.R.*, 1960, **133**, 386.

[12] Amerthaligam, Padmanabhan, and Shankar, *Acta Cryst.*, 1960, **13**, 20.

[13] Fackler, Jr., Ph.D. Thesis, Massachusetts Institute of Technology, 1960.

[14] Kitson and Griffith, *Analyt. Chem.*, 1956, **24**, 334.

[15] Lippert and Vogel, *Z. phys. Chem.* (*Frankfurt*), 1956, **9**, 133.

[16] Skinner and Thompson, *J.*, 1955, 487.

[17] Gallo and Sensi, *Ann. Chim.* (*Italy*), 1956, **46**, 816.

Cyanide stretching frequency of metal complexes of 3-cyanopentane-2,4-dione.

Metal	M. p.	Solvent	$\lambda_{max.}$ (cm.$^{-1}$) [a]	$10^2\varepsilon$ (l. mole^{-1} cm.$^{-1}$)/CN
Fe(III)	244°	$CHCl_3$	2216·0	3·8
Cr(III)	290 (subl.)	$CHCl_3$	2216·3	3·3
Co(III)	Decomp.	$CHCl_3$	2216·6	3·2
Al(III)	290 (subl.)	$CHCl_3$	2217·2	3·5
Ga(III)	268	$CHCl_3$	2217·5	3·2
In(III)	244	$CHCl_3$	2215·4	3·4
Be(II)	251	$CHCl_3$	2220·5	3·6
		KBr	2218·7	
Cu(II)	Decomp. >250	$CHCl_3$ [b]	2212·5	—
		KBr	2196·2 [c]	
Th(IV)	—	$CHCl_3$ [b]	2211·6	—
		KBr	2211·9 [d]	
H	—	$CHCl_3$	2220·4	2·7
		KBr	2218·9	
Zn(II)	Decomp.	KBr	2225·4	
VO,H_2O	Decomp.	KBr	2216·3	
K	—	KBr	2187·9	

[a] Half-width at half-height ~13 cm.$^{-1}$; spectra (in $CHCl_3$) reproducible to $\pm 0·5$ cm.$^{-1}$. [b] Saturated solution at 25°. [c] Peak also at 2207·1 cm.$^{-1}$. [d] Shoulder at 2220 cm.$^{-1}$.

With the exception of the gallium(III) and indium(III) complexes, all the trisacetylacetonates of the metal ions used in this study are known to be octahedral.* It is believed that the tris-complexes of 3-cyanopentane-2,4-dione are also octahedral with respect to the positions of the six oxygen atoms. The frequency and intensity of the C≡N stretch (Table) for these six-co-ordinate complexes was found to be almost completely independent of the metal ion in the complex. In view of the shifts noted in the C≡N stretch of aromatic nitriles on *para*-substitution, it is difficult to accept the possibility that the vibration is not sensitive to perturbations of the chelate ring by the metal ion. In appears from these results that metal–oxygen bonding in trisacetylacetonates of iron(III), chromium(III), and cobalt(III) is not significantly different from bonding in the so-called "outer orbital" complexes of aluminium(III), gallium(III), and indium(III). The extent to which the $2p_\pi$-electrons on the chelate ring are affected by interaction with the $3d$-orbitals of transition-metal ions in these complexes appears to be small, if this effect exists at all here. The interaction is considerably less than that between the $2p_\pi$-electrons in benzene and substituents with $2p$-orbitals.

Substantially no shift is observed in the C≡N stretch when beryllium(II) replaces hydrogen in 3-cyanopentane-2,4-dione, while shifts of ~4 cm.$^{-1}$ are observed in the tris-complexes. The complexes with copper(II) and thorium(IV) show a bathochromic shift of ~8 cm.$^{-1}$. The overall effect produced by replacing hydrogen by a metal is small and this is perhaps to be expected if the ligand exists primarily as the hydrogen-bonded enol in chloroform and the interaction of metal orbitals with the $2p_\pi$-electrons of the chelate ring is not extensive. It is hazardous to attribute the shifts observed in the copper(II) and thorium(IV) complexes to changes in metal–oxygen bonding from the limited results at present available. The symmetry of the oxygen atoms around the metal atom is different in each of these cases. A study of other complexes having similar geometries is necessary before generalizations can be made.

Also included in the Table are the positions observed for the C≡N stretch in KBr disc spectra of the vanadyl, zinc(II), potassium, copper(II), and thorium(IV) complexes. Disc spectra of the tris-complexes often showed peculiarities, and in three cases, copper(II), thorium(IV) and iron(III), the band was split. Splittings presumably can be attributed to solid-state interactions on the C≡N groups. The unusually low frequency observed

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* While the overall symmetry of the tris-chelate complexes is not O_h, but rather D_3, the extent to which this trigonal component affects the electronic properties of the complex is at present a subject of considerable concern.[18]

[18] Piper, 140th Meeting of Amer. Chem. Soc., Chicago, Ill., Sept., 1961; Orgel, *J.*, 1961, 3683.

for the C≡N stretch of the potassium salt is interesting but not readily interpreted without additional study.

EXPERIMENTAL

Traube[19] reported that cyanogen reacts with acetylacetone to produce a compound described as " cyano-imido-methylacetylacetone." This material was subsequently hydrolyzed to 3-cyanopentane-2,4-dione. Traube describes the β-diketone as strongly acidic but does not describe the preparation of any metal complexes.

3-Cyanopentane-2,4-dione.—Pentane-2,4-dione (50 g., 0·5 mole; from Distillation Products) was added to sodium (~0·5 g.) in absolute ethanol (200 ml.) which was stirred under dry nitrogen and cooled at 0°. Cyanogen, from copper(II) sulphate pentahydrate (500 g.) and aqueous potassium cyanide, was bubbled through the solution. The exit gases passed through sodium hydroxide solution.

The " imido "-product * was filtered with suction from the alcohol and immediately treated with sodium hydroxide (60 g.) in cool water (~500 ml.). After dissolution was complete, ice was added and the mixture neutralized with 6N-hydrochloric acid. The β-diketone crystallized. The yield of product depended on the treatment of the " imido " intermediate before hydrolysis. This intermediate decomposed rapidly on storage, leaving a brown material which was not readily separated from the final product. A maximum yield of ~90%, based on pentane-2,4-dione, was obtained. The β-diketone was purified by precipitation as the copper(II) complex with aqueous copper(II) acetate and subsequent decomposition of the complex in dilute sulphuric acid. The β-diketone recrystallized from 1 : 6 : 30 acetone–ethanol–water (Found: C, 58·2; H, 5·9. Calc. for $C_6H_7NO_2$: C, 57·8; H, 5·7%).

Metal Complexes.—The chelate *complexes* of 3-cyanopentane-2,4-dione listed in the Table were prepared by methods described for complexes of pentane-2,4-dione.[21] The complexes, except the potassium salt, were analysed for carbon and hydrogen with the results tabulated here

	Required (%)		Found (%)			Required (%)		Found (%)	
Metal	C	H	C	H	Metal	C	H	C	H
Fe(III) ...	50·5	4·2	50·3	4·1	Be(II) ...	56·2	4·7	56·0	4·7
Cr(III) ...	51·0	4·1	51·1	4·1	Cu(II) ...	46·2	3·9	46·9	4·1
Co(III) ...	50·2	4·1	51·1	4·4	Th(IV) ...	39·6	3·3	38·9	3·5
Al(III) ...	54·2	4·5	54·6	4·5	Zn(II) ...	46·0	3·8	46·8	4·3
Ga(III) ...	48·9	4·1	51·0	4·5	VO,H_2O	43·4	4·2	43·9	4·2
In(III) ...	44·4	3·6	43·0	3·8					

Infrared Spectra.—The spectra were recorded on a Perkin–Elmer model 21 spectrophotometer with a calcium fluoride prism. The instrument was calibrated with CO_2(g), NH_3(g), and polystyrene. The CN stretching frequencies observed for acetonitrile in chloroform were found within ±0·5 cm.$^{-1}$ of recorded values.[22] Since the bands observed have half-widths at half-height of ~13 cm.$^{-1}$ in chloroform, it is believed that the recorded maxima are accurate to slightly better than ±1 cm.$^{-1}$. Chloroform solutions were observed at two concentrations, with the exception of the copper(II) and thorium(IV) complexes which were only slightly soluble. The frequencies appeared to be independent of concentration and only slight variations in intensity were noted.

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* The " cyano-imido-methylacetylacetone " is described by Traube as white crystals, $(CH_3{\cdot}CO)_2C(CN){\cdot}CH{=}NH$. It shows no infrared spectral bands in the region 3·5—5·8 μ. The CN stretch intensities may be considerably weakened by electro-negative groups in the molecule. The chemical properties suggest that the compound[20] may be 3,4-dicyanopent-2-ene-2,4-diol.

[19] Traube, *Ber.*, 1898, **31**, 2944.

[20] Noyce, personal communication.

[21] See Vols. **2**, **5**, and **6** of *Inorg. Synth.*

[22] Felton and Orr, *J.*, 1955, 2170.