

CCA-293

546.621:546.681:547.442.3.07:544.621

Original Scientific Paper

Aluminium(III) and Gallium(III) Tris- γ -Nitroacetylacetonates. Preparation and Infrared Spectra*

C. Djordjević

Institute »Ruđer Bošković«, Zagreb, Croatia, Yugoslavia

Received February 19, 1963

Aluminium(III) and gallium(III) derivatives of γ -nitro-2,4-pentanedione have been prepared by electrophilic substitution of the hydrogen on the chelated acetylacetonone molecule. Infrared spectra of these new metal complexes have been studied. On comparison with the spectra of analogous derivatives of some divalent metals and spectra of aluminium(III) and gallium(III) tris-acetylacetonates the assignment of some characteristic vibrational frequencies is given. Additional modes of the nitro-group and the metal-oxygen vibrational modes are discussed in more details.

Recently it has been reported^{1,2} that metal acetylacetonates of some divalent transition metals and aluminium(III) react in benzene solution with gaseous dinitrogen tetroxide. From the reaction products bis- γ -nitro-acetylacetonone metal derivatives can be isolated. The aim of this investigation was to see whether octahedral metal acetylacetonates of trivalent non-transitional metals behave in a similar way, and if so, to analyse the infra-red spectra of these compounds. It is of interest to know how the group frequencies of the nitro-group present shift on comparison with the planar derivatives of divalent transition metals² and what information can be obtained from the related metal-oxygen vibrational bands.³

EXPERIMENTAL

Tris-acetylacetonate Al(III) and tris-acetylacetonate Ga(III) were prepared according to the literature.

Tris- γ -nitro-acetylacetonate aluminium(III)²

Al(III) acetylacetonate was dissolved in dry benzene. Gaseous dinitrogen tetroxide was introduced in the solution at room temperature. The gas was absorbed and when no further absorption of the gas was perceived, the reaction was stopped. The excess of dinitrogen tetroxide was removed on a pump and the reaction product filtered. Petrol ether was added to the filtrate and a fine pale yellow precipitate was obtained. M.p. 190°.

Anal. GaC₁₅H₁₈N₃O₂₁ calc'd.: Al 5.9; C 39.2; H 4.0; N 9.8%
found: Al 5.3; C 40.1; H 4.1; N 9.2%

The compound is soluble in some organic solvents, but not in water. It ignites spontaneously on heating in air.

* Reported at I. Yugoslav Congress of Pure and Applied Chemistry, Zagreb, 1960, Abstract of papers p. 10.

*Tris-γ-nitro-acetylacetonate aluminium(III)*²

Ga(III) acetylacetonate was dissolved in dry benzene. Dinitrogen tetroxide was introduced in the solution as in the preparation of aluminium compound. A yellow complex was obtained in the same way, by precipitating with the petrol ether. Beautiful long needles were obtained. M.p. 219°.

Anal. $\text{GaC}_{15}\text{H}_{18}\text{N}_3\text{O}_{12}$ calc'd.: C 35.9; H 3.6; N 8.4%
found: C 36.3; H 4.2; N 8.7%

The compound is soluble in some organic solvents, but not in water and alcohol. It ignites spontaneously in air on heating.

Infra-red spectra were recorded with a Perkin-Elmer spectrometer model 221, equipped with a NaCl and KBr prism. The samples were examined in the solid state as nujol mulls and in KBr disc.

X-ray examinations. Powder diffraction photographs were taken by using nickel filtered Cu-K radiation. The specimens were prepared in a Lindemann glass tube of 0.3 mm diam.

RESULTS

It has been found that from the reaction of aluminium(III) and gallium(III) acetylacetonates with gaseous dinitrogen tetroxide in benzene solution crystalline yellow compounds can be isolated. The analysis of the substances obtained agrees well with the formula $\text{M}^{\text{III}}(\text{C}_5\text{H}_6\text{NO}_4)_3$. The complexes are soluble in chloroform and acetone and insoluble in benzene, ether and alcohol. In water they slowly decompose, as well as in a moist atmosphere, but in a

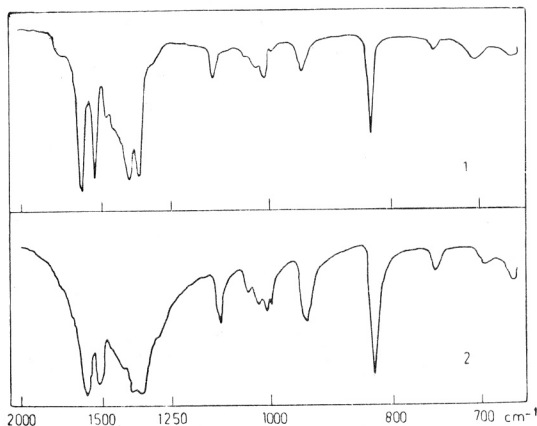


Fig. 1. Infra-red spectra of aluminium(III) and gallium(III) tris- γ -nitro-acetylacetonate in NaCl region.

dessicator they can be kept unchanged. X-ray powder photographs have shown that the nitro-complexes are not isomorphous with parent acetylacetonates, as expected. Moreover, from a dense and complicated diffraction pattern it seems that the nitro-acetylacetonates of trivalent aluminium and gallium are not isomorphous, while the simple acetylacetonates are known to be isomorphous.⁴

The infra-red spectra have proved to be useful in determining the place of substitution in divalent acetylacetonates.² The same expected characteristic features are observed in the spectra of trivalent metal complexes as well. The spectra are shown in Fig. 1. and Fig. 2. In the Table I. the

TABLE I
IR Frequencies in cm⁻¹

Al(C ₅ H ₇ O ₂) ₃	Ga(C ₅ H ₇ O ₂) ₃	Al(C ₅ H ₆ O ₂ NO ₂) ₃	Ga(C ₅ H ₆ O ₂ NO ₂) ₃	Assignment
1595 s { 1548 1534 s	1587 s 1534 s	1597 s 1534 s	1587 s 1524 s	C≡C, C≡O stretchings
{ 1446 1429 1395 s	1406 { 1385 s — 1285 s	1479 m { 1449 1416 1389 s 1351 s	{ 1471 m 1408 1385 s 1348 s	v ₁ -fundamental, NO ₂ asym. stretch. C≡O stretch., C—H def. v ₃ -fundamental, NO ₂ sym. stretch. C≡C stretch. + C—CH ₃ stretch.
1193 w —	1198 w —	— 1126 m	— 1111 m	Ring C—H in plane def. C—N mode
{ 1029 m 1018 937 s	1024 m 937 m	{ 1053 vw 1029 w 1008 m 938 m	{ 1046 w 1022 m 1005 m 922 m	CH ₂ rocking, C—CH ₃ + C≡ stretch. C—CH ₃ stretch.
— { 787 776 m 772	— { 799 781 m	825 s — 753 w	825 s — 761 w	v ₂ -fundamental, ONO in plane def. Ring C—H out of plane def.
{ 686 s 657 s 594 577 s	{ 682 s 655 s	{ 702 690 m 667 616 m 592	{ 697 w 669 m 605 m	Ring def. + M—O vibration modes + C—CH ₃ def.
{ 496 s 489 482	— { 514 s 503 s 489 vs	{ 514 s 503 s 489 vs	{ 466 m 444 426 w 412 w	Metal—oxygen stretching modes
425 w 414 w	446 m 425 w 414 w	431 w 421 w	— 426 w 412 w	Ring deformation modes

vibrational frequencies of the tris- γ -nitro-acetylacetonates of aluminium(III) and gallium(III) are listed in comparison with the frequencies of parent metal acetylacetonates. Characteristic additional bands found in the spectra of metal nitro-acetylacetonates are assigned as fundamentals of the nitro-group and the C-N vibrational mode. Bands related to the ring C-H vibrational modes, found in the spectra of aluminium(III) and gallium(III) acetylacetonates at 1193 and 1198 cm^{-1} , respectively, are absent in nitro-chelates. In the range of metal-oxygen vibrational modes additional bands are observed in nitro-derivatives. The first band in this group of bands is found at a higher frequency than in the parent acetylacetonates.

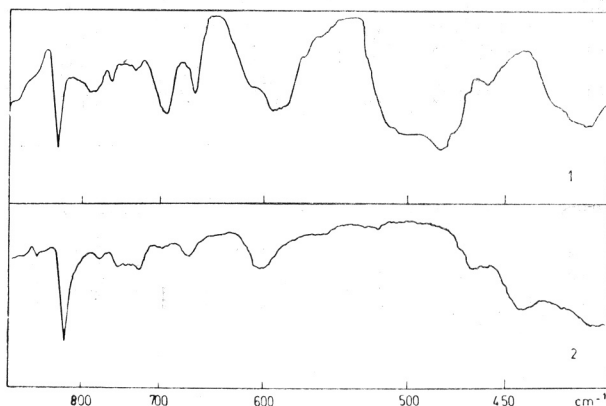


Fig. 2. Infra-red spectra of aluminium(III) and gallium(III) tris- γ -nitroacetylacetonate in KBr region.

DISCUSSION

The C_{2v} symmetry of the acetylacetonate ring is lowered in the case of the nitro-chelate ring, because the presence of the methyl groups in the ortho position forces the nitro-group to rotate somewhat about the C-N bond. The oxygen atoms are expected to be twisted out of the ring plane as for example in nitrodurene.⁵ Characteristic vibrational frequencies which are expected in nitro-acetylacetonate chelate system are in the first place frequencies of the parent ring system, already extensively studied on metal acetylacetonate complexes^{3,6,7,8} Further on additional vibrations of the nitro-group must appear.^{2,9} The main differences in the spectra of the new chelated molecule on comparison with the simple acetylacetonate ring are expected to be: a) the absence of vibrational modes of the ring hydrogen, the $\geq C-H$ group, b) new additional bands, due to the fundamentals of the nitro-group, as well as the modes of the C-N bond, c) characteristic shifts of some frequencies due to altered electron distribution in the ring, caused by the polarity of the nitro-group, and by the mass effect of this group, d) changes in the absorption region of the metal-oxygen stretching vibrational modes, at the low wave length region. This is of special interest, because it reveals informations on the nature of the metal-ligand bonds.^{2,3,8,9} Some differences are also expected in skeletal deformation modes, present in this region.

The deuteration studies on cupric acetylacetonate² enabled the assignment of ring hydrogen vibrations. It has been found that the corresponding bands are not present in the spectra of tris- γ -nitro-acetylacetonates. (See Table I.) Characteristic additional bands are found in the spectra of metal nitro-acetylacetonates on comparison with simple metal acetylacetonates at 1479, 1351, 1126, 825, and 1471, 1384, 1111, 825 cm^{-1} for aluminium (III) and gallium(III) derivative, respectively. The assignment given in Table I. is based on the spectra of the compounds containing nitro-group^{6,10,11} and the spectra of related acetylacetonates^{3,7,8}. Frequency of 825 cm^{-1} is particularly characteristic for all nitro-acetylacetonate complexes. This band is assigned as predominantly ν_2 fundamental of the nitro-group, the O—N—O bending. It is notable that this band does not shift with the change of the metal, nor even in passing from planar² to octahedral complexes. Such behaviour indicates that the resonance of the chelate system, if extended on the nitro-group, does not depend much upon the metal atom. Little systematic work has yet been done to identify the modes of the C—N bond. In different type of compounds bands in the region 1350—1030 cm^{-1} have been proposed.⁶ The bands at 1126 and 1111 cm^{-1} for aluminium(III) and gallium(III) complex respectively, are assigned as a C—N vibrational mode. Changes in the region of 1300—600 cm^{-1} are observed. Their origin are probably additional skeletal and different deformation modes, coupled to certain extent with other vibrations, the shifts of some frequencies arising from the ring environment alteration, caused by the nitro-group presence.

The most significant changes observed on comparing the spectra of the new and parent chelate system are observed in the region of metal-oxygen vibrations, below 500 cm^{-1} . Mass effect of the metal, the nature of the metal-oxygen bonds and the coupling of several M—O bonds are the essential factors responsible for the peculiarities in this part of the spectra. Skeletal deformation modes, including ring nitro-group, are also reflected in this spectrum range. The octahedral aluminium and gallium tris- γ -nitro-acetylacetonates show differences in the spectra due to the mass effect in the first place.^{3,8} The metal sensitiveness of the bands shows that they certainly belong to a metal-oxygen active mode and are not originated in the vibrations of the sole ligand. Derivatives of aluminium and gallium, non-transitional metals of the same valence orbital electronic configuration are expected to behave similarly in these chelates, forming analogous metal-ligand bonding, and shift of the metal sensitive bands in the infra-red spectra is therefore mainly due to the mass effect.³ Additional bands found in this range at slightly higher frequencies, on comparison with corresponding acetylacetonates are metal sensitive and in general broad and not well resolved. They can be understood in the first place in view of couplings of the six metal-oxygen bonds in an octahedral complex, with a situation even more involved in nitro-derivatives, where owing to the lower symmetry of the molecule, splitting of some modes may arise. It is significant, however, that the first band in metal oxygen vibration region appears in the nitro-acetylacetonato complexes always at a higher frequency^{2,8,9}. In aluminium(III) and gallium(III) derivatives the first metal-oxygen vibrational band is about 20 cm^{-1} higher than in the corresponding parent acetylacetonates. The position of this frequency may indicate a relatively greater participation of nitro-acetylacetonato-ligand as electron donor in the bond formation. However, a shift of this

magnitude implies that the bond order of the metal-oxygen band in the nitro-acetylacetonates remains approximately same as the bond order of the related acetylacetonates. Therefore the nature of the metal-ligand bond does not change essentially on replacing the ring hydrogen of the acetylacetonato chelate with the nitro-group.

Acknowledgement. The author is grateful to Prof. D. Grdenić and Dr. M. Randić for discussion and thanks B. Korpar and O. Hadžija for microanalyses.

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IZVOD

Aluminij(III) i galij(III) tris- γ -nitro-acetilacetonati. Priprema i infra-crveni spektri

C. Djordjević

Priređeni su aluminij(III) i galij(III) derivati γ -nitro-2,4-pentadiona. Reakcija metalnih acetylacetonata sa N_2O_4 u benzenskoj otopini dovodi, kao i u slučaju nekih dvovalentnih metalnih acetylacetonata, do elektrofilne supstitucije vodika u γ -položaju sa nitro-skupinom. Analizirani su infra-crveni spektri ovih novih metalnih kompleksa. Na osnovu usporedbe ovih spektara sa spektrima analognih derivata nekih dvovalentnih metala i aluminij(III) i galij(III) tris-acetylacetonata, izvršena je asignacija karakterističnih vibracionih frekvencija. Vibracioni modusi nitro-grupe i veze metal-kisik diskutirani su detaljnije. Utvrđeno je, da je konstantna apsorpcija kod 825 cm^{-1} , koja odgovara deformaciji ONO skupine, karakteristična za γ -nitro-acetylacetonate dvo- i tro-valentnih metala, ukazujući na to da rezonancija helatnog sistema — ukoliko se proteže na nitro-skupinu, ne ovisi mnogo o metalnom atomu.

INSTITUT »RUĐER BOŠKOVIĆ«
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Primljeno 19. veljače 1963.