934. *The Reactivity of Co-ordinated Acetylacetone.*

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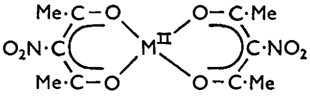
The reactivity of acetylacetone, co-ordinated to a metal atom, with various reagents has been investigated. The complexes of copper, nickel, platinum, and aluminium yield γ-nitro-substituted complexes with dinitrogen tetroxide. Nitrosyl chloride yields nitroso- or chloro-complexes depending on the conditions employed. Nitrite ions in the presence of ammonia at pH 7 yield iminoacetylacetone derivatives of nickel and palladium; these are typical diamagnetic, square complexes. The structure of the complexes has been investigated by a variety of physical techniques; in particular, infrared spectra have been used extensively to identify the substituted groups present and to assign structures to the complexes isolated. Several unusual types of synthetic organic reaction dependent on the fact that the acetylacetone is co-ordinated to a metal atom have been identified.

The co-ordination of a metal to an organic molecule, may alter radically the reactivity of the organic portion. This change can arise from three main sources: (i) co-ordination of the metal may change the electronic distribution within the molecule; (ii) co-ordination invariably binds a chemically active centre of the molecule; and (iii) the organic molecule may be forced into a specific stereochemical form.

In order to investigate the reactivity of organic molecules on co-ordination, we have studied the variations in the reactivity of acetylacetone on co-ordination. We have briefly reported[1] the nitration of the acetylacetone ring in the case of the copper complex, by dinitrogen tetroxide in benzene solution. Subsequent work by Kluiber[2] and Collman *et al.*[3] has shown that some halogenations can be carried out with metal complexes of acetylacetone and related ligands. We report here the reactions of metal–acetylacetone complexes towards dinitrogen tetroxide, nitrosyl chloride, and nitrite ions, and it is convenient to discuss the results with respect to these reagents in turn.

(*a*) *Dinitrogen Tetroxide.*—Dinitrogen tetroxide was found to react with copper, nickel, platinum, and aluminium acetylacetonate in benzene or chloroform solutions, to yield nitro-derivatives; in the case of palladium an impure product containing a similar nitro-derivative was obtained. Dinitrogen tetroxide may be considered to react with a metal acetylacetonate in three ways: (i) substitution in the ligand; (ii) oxidation of the metal and/or ligand; (iii) formation of nitrite complexes of the metal. In substitution of the acetylacetone, reaction may occur either at the methyl groups or at the γ-CH group, provided no fission of the metal–oxygen bond occurs. It has been found that with the bivalent-metal acetylacetonates substitution appears to occur on the central (γ-) carbon of the acetylacetone, yielding complexes of type (I). With aluminium, it has been possible to isolate the di- and the tri-nitro-derivative. The evidence in favour of the formulation is summarised for the individual metals.


(I)

Copper. When bisacetylacetonatocopper(II) is treated with dinitrogen tetroxide in benzene or chloroform one obtains a green crystalline compound $Cu(C_5H_6O_2{\cdot}NO_2)_2$. This is stable in air at room temperature, but ignites spontaneously when heated. The magnetic

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[1] Djordjević, Lewis, and Nyholm, *Chem. and Ind.*, 1959, 122.
[2] Kluiber, *J. Amer. Chem. Soc.*, 1960, **82**, 4839.
[3] Collman, Moss, Maltz, and Heindel, *J. Amer. Chem. Soc.*, 1961, **83**, 531.

susceptibility at room temperature confirms the presence of bivalent copper ($\mu_{\text{eff}} =$ 2·0 B.M.). After alkaline hydrolysis of the compound, no nitrite was detected in the solution, strongly suggesting that the substitution had taken place on the ligand. Molecular-weight studies, both isopiestic in acetone and ebullioscopic in chloroform, show that the complex is a monomer in these solvents.

Nickel. Treatment of bisacetylacetonatonickel(II) * with dinitrogen tetroxide in benzene solution yields a green complex. The reaction is not as straightforward as for case of copper, side-reactions decreasing the yield of the nitroacetylacetone compound. However, careful purification yielded the compound as olive-green leaflets. The complex is sensitive to moisture and less stable than the corresponding cupric derivative. The magnetic moment ($\mu_{\text{eff}}=$ 3·3 B.M.) is similar to those of related nickel chelate derivatives and indicates the presence of a bivalent spin-free nickel complex. As with the parent nickel–bisacetylacetone compound, the product is very hygroscopic and the analytical values indicate that it is a mixture of the nitroacetylacetonate and the hydrated complex.

Platinum. When bisacetylacetonatoplatinum(II) is treated with dinitrogen tetroxide under the same conditions in benzene a yellow crystalline compound is produced. Insolubility prevents recrystallisation, but analysis agrees with the formula $Pt(C_5H_6O_2{\cdot}NO_2)_2$, showing that practically no side-reactions take place.

Palladium. Bisacetylacetonatopalladium(II) reacts with dinitrogen tetroxide in benzene in a similar manner to the other metal complexes. However, attempts to obtain the analogous dinitroacetylacetonatopalladium(II) in a pure form failed. With copper and nickel, the nitroacetylacetonates have been obtained pure by recrystallisation as the solubility of the metal nitroacetylacetonates allows separation from the insoluble by-products. However, owing to its insolubility, the palladium derivative cannot be separated from the products of side-reactions.

Aluminium. An excess of dinitrogen tetroxide with trisacetylacetonatoaluminium(III) in benzene gives a pale yellow product, $(C_5H_6O_2{\cdot}NO_2)_3Al$. The molecular weight, determined isopiestically in acetone, shows that the complex is monomeric; in agreement with this the compound is a non-electrolyte in nitrobenzene and nitromethane.

Use of smaller quantities of dinitrogen tetroxide leads to partially nitrated complexes. With 1 mol. of metal complex and 3 mol. of dinitrogen tetroxide a disubstituted product $Al(C_5H_6O_2{\cdot}NO_2)_2,(C_5H_7O_2)$ was isolated. Comparison of the powder photographs of this compound with those of trisacetylacetonatoaluminium(III) and tri(nitroacetylacetonato)-aluminium(III) showed the product was not a mixture of these two compounds. Attempts to prepare the nitroacetylacetonates of iron(III) and chromium(III) by this procedure yielded a series of intractable products that were not investigated.

Infrared spectra. The main evidence for the structure of these nitro-compounds comes from their infrared spectra. The infrared spectra of metal acetylacetonates have been extensively studied,[4] but in order to establish those vibrations associated with the γ-CH group we have investigated the spectra of compounds deuterated in this position. Bratož *et al.*[5] examined deuterated acetylacetone and assigned a band at 1192 cm.$^{-1}$ to a γ-CH deformation frequency. No work has been reported on the complexes of the deuterated ligand. Previous studies on the deuteration of metal acetylacetonates by Nesmeyanov *et al.*[6] have shown that, with cobalt(III) and aluminium(III) acetylacetonate, exchange with deuterium oxide in dioxan does not take place during 20 hours; we have also shown that no deuteration of bisacetylacetonatocopper(II) occurred over periods up to two weeks.

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* This name is without prejudice to the molecular complexity; the compound is a trimer in the solid state but is partially depolymerised in solution.

[4] See Cotton, " Modern Coordination Chemistry," Interscience Publ., Inc., New York, 1960.

[5] Bratož, Hadži, and Rossmy, *Trans. Faraday Soc.*, 1956, **52**, 464.

[6] Nesmeyanov, Kursahov, Smolina, and Parnes, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1949, 598.

The deutero-complex was prepared, therefore, from deuterated acetylacetone and a copper salt in D_2O solution.

From a comparison of the deuterated and the normal complex, the following differences in the spectra may be noted. (1) In the region 1600—1500 cm.$^{-1}$, the first strong band, assigned by Nakamoto *et al.*[7] as a C=C stretching frequency, is not affected, but the other two strong bands, assigned severally as a perturbed carbonyl stretching frequency and a C–H deformation frequency, appear to be deuterium-sensitive. On deuteration these bands are shifted to lower wavelengths, possibly owing to the mass effect of the deuterium on the γ-carbon of the ring system [the small isotopic effect ($\nu_H/\nu_D = 0{\cdot}981$) implies that this is not a pure carbon–hydrogen vibration]. (2) A characteristic shift of the frequency at 1192 cm.$^{-1}$ is observed on deuteration. This band is assigned to the C–H in-plane deformation. The new band, due to the γ-C–D deformation, is very well resolved, appearing at 918 cm.$^{-1}$ ($\nu_H/\nu_D = 0{\cdot}769$). (3) Another deuterium-sensitive frequency is the band appearing in the parent complex at 781 cm.$^{-1}$. This is shifted in the deuterated complex to 581 cm.$^{-1}$ ($\nu_H/\nu_D = 0{\cdot}744$). According to this evidence the band is assigned as the out-of-plane γ-C–H deformation, which is expected in this region of the spectrum.[7] (For benzene the out-of-plane vibration mode occurs in the region 900—700 cm.$^{-1}$.) (4) At the lower frequencies of the spectrum, one finds that the copper–oxygen mode is unchanged. A weak band at 430 cm.$^{-1}$ for cupric acetylacetonate is only slightly deuterium sensitive ($\nu_H/\nu_D = 0{\cdot}990$), being shifted after the isotopic substitution to 426 cm.$^{-1}$. The band probably represents a skeletal deformation mode, which certainly should be deuterium-sensitive.

The major frequencies of the product of reaction and the parent acetylacetonate, are given in Table 1. The following observations can be made from the spectra: (i) In the products, bands characteristic of the nitro-group are evident. (ii) The bands assigned as γ-CH vibrations, from the deuteration studies, are absent for the products, indicating that the nitro-group has entered this position. (iii) Frequency changes occur in the region normally associated with the C–O and C=C stretching vibrations. This may arise from the influence of the nitro-group on the resonance in the ring system, and also from the mass

TABLE 1.

Characteristic infrared frequencies in metal acetylacetonates and corresponding metal nitroacetylacetonates.

Compound	C–O, C=C stretch and C–H defn.	NO_2		CO	C–H in-plane defn.	C–D in-plane defn.	NO_2 out-of-plane	M–O and skeletal modes
$Cu(C_5H_7O_2)_2$	1582, 1553, 1531	—	—	1353	1192	—	—	452 ± 2 430 ± 2
$Cu(C_5H_6DO_2)_2$	1582, 1527, 1506	—	—	1353	—	918	—	454 ± 2 426 ± 2
$Cu(C_5H_6O_2{\cdot}NO_2)_2$ ...	1585, 1522	1479	1370	1337	—	—	827	460 ± 2 446 ± 2
$Ni(C_5H_7O_2)_2$	1592, 1524	—	—	1404	1193	—	—	438 ± 2
$Ni(C_5H_7O_2)_2,2H_2O$	1698, 1675, 1608, 1513	—	—	1404	1199	—	—	430 ± 2
$Ni(C_5H_6O_2{\cdot}NO_2)_2$ ...	1672, 1610, 1520	Not resolved	1328	—	—		825	444 ± 10
$Pd(C_5H_7O_2)_2$	1562, 1541, 1517	—	—	1353	1196		—	464 ± 2 441 ± 2
$Pd(C_5H_6O_2{\cdot}NO_2)_2$ ...	1727, 1672, 1623, 1524	1425	1370	1330	—		826	468 ± 10
$Pt(C_5H_7O_2)_2$	1567, 1536	—	—	1372	1205		—	475 ± 2 448 ± 2
$Pt(C_5H_6O_2{\cdot}NO_2)_2$ ...	1548, 1529	1488	1370	1342	—		826	490 ± 2 460 ± 2

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[7] Nakamoto and Martell, *J. Chem. Phys.*, 1960, **32**, 588.

effect of the nitro-group compared with hydrogen. (iv) It has been suggested that the metal–oxygen modes, occurring in the low-frequency region of the spectrum, decrease in the order of the stability constants of the complexes.[8] The metal–oxygen frequencies given for the parent acetylacetonates agree with previous data; from the location of the band in the platinum complex, the compound appears to have a stability constant higher than those of the corresponding nickel and palladium complexes. It is of interest that the corresponding frequencies for the nitro-compounds shift towards higher frequencies and follow the order Ni $<$ Cu $<$ Pd $<$ Pt. (v) The spectrum of the partially substituted aluminium complex shows features characteristic of the spectra of both the parent complex and the fully nitrated compound. The intensity of the vibrations associated with the γ-CH and the nitro-group are in agreement with the replacement of two of the hydrogen atoms of the parent compound by nitro-groups.

(*b*) *Nitrosyl Chloride.*—Nitrosyl chloride reacts with organic compounds to produce nitroso-, nitrito-, or chloro-compounds, depending on the conditions. The metal acetylacetonate complexes of copper, nickel, and platinum were observed to react with nitrosyl chloride in benzene.

From the copper complex, a precipitate of cupric chloride is the main product; from the nickel complex, a derivative that is either an oxime or a nitroso-compound was obtained, but its analyses were not reproducible. However, bisacetylacetonatoplatinum(II) gave a yellow compound, $Pt(C_5H_8O_2Cl)_2$, only very slightly soluble in organic solvents and insoluble in water. This complex is very stable, and inert to the majority of chemical reagents. The structure suggested is based solely on the infrared spectrum as the complex is too insoluble to allow investigation by the normal techniques. The characteristic γ-CH vibrations are absent from the infrared spectrum of this complex, suggesting substitution by the chlorine in this position of the acetylacetone. Except for appearance of a band at 1661 cm.$^{-1}$ only slight changes are observed in the spectrum in 1500—1700 cm.$^{-1}$ region. A new band appears at 721 cm.$^{-1}$ and this may be assigned to a C–Cl stretching vibration. The infrared spectrum thus indicates that substitution by chlorine has occurred on the γ-CH of the acetylacetone.

It is somewhat surprising that reaction with nitrosyl chloride yields a chloro- rather than a nitrito-derivative or nitroso-complex, as chlorination of organic compounds normally occurs only at elevated temperatures. However, nitrosyl chloride readily dissociates to nitric oxide and chlorine, and chlorination may well be due to this dissociation. The purity of the product, in the case of the platinum salt and in marked contrast to the nickel and copper reactions, may be associated with the insolubility of the platinum chloroacetylacetonate.

(*c*) *Nitrite Ions.*—The reactions of bivalent nickel, palladium, platinum, and copper acetylacetonates with nitrite ions, in the presence of ammonium acetate, have been investigated in water, alcohol, or water–alcohol. The pH of the solution under these conditions is about 7.

In these circumstances bisacetylacetonatonickel(II) forms a bright red compound, $Ni(C_5H_7O_2N_2)_2$. This is diamagnetic, soluble in organic solvents, and monomeric in chloroform; it is a non-electrolyte in nitrobenzene. The presence of ammonia is essential for formation of this compound.

Experimental conditions were varied so as to afford the best way of preparing the complex. The compound may be prepared from bisacetylacetonatonickel(II) or a nickel salt; indeed the simplest method involves starting with nickel acetate in the presence of ammonium acetate. Attempts to prepare the complex in the absence of ammonia, at pH 7, were unsuccessful, suggesting that ammonia plays an essential part in the reaction.

The corresponding palladium(II) derivative was obtained in similar conditions. This compound is also diamagnetic, but it is less soluble in the organic solvents than the nickel

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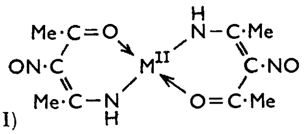
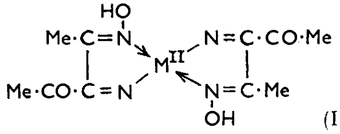
[8] Nakamoto, McCarthy, and Martell, *Nature*, 1959, **183**, 459.

compound. In similar experiments with bivalent copper and platinum no reaction occurred.

Two possible structures for the nickel and palladium complexes are (II) and (III), the imino-group being derived from the ammonia. In order to differentiate between these a study was made of infrared spectra. The spectra of the nickel and the palladium compound are almost identical, the characteristic frequencies being listed in Table 2. These differ from those of the corresponding metal acetylacetonate. A new band is found at 3236 cm.$^{-1}$ for the nickel and 3247 cm.$^{-1}$ for the palladium compound. In the proposed structures this frequency can be assigned either as an NH or an OH stretching frequency. In the latter case the low frequency can be attributed to hydrogen bonding. In addition, new bands also appear in the 1700—1600 cm.$^{-1}$ region, which is potentially the most informative about electronic distribution in the chelate system. The frequencies can be assigned as a perturbed C=O stretch, C=C, N=O, or C=N stretching frequencies, or N–H or C–H deformation frequencies. The general analysis of the infrared spectra is thus compatible with both proposed structures. However, the frequencies appearing in this region are high for a perturbed C=O stretching frequency, as normally observed in metal acetylacetonates and expected for structure (I). The high values of the frequencies agree with a vibration of an unperturbed keto-group, which would be present in structure (II). Two well-resolved frequencies appear in the 500 cm.$^{-1}$ region, where metal–nitrogen modes are expected.[9] These are at 537 and 524 cm.$^{-1}$ in the case of the nickel, and 511 (not well resolved) and 498 cm.$^{-1}$ in the case of the palladium complex. In both structural alternatives, two metal–nitrogen modes may arise. For structure (II) this would imply a *cis*-arrangement of the ligands. In the lower region a very weak band at 462 cm.$^{-1}$ is obtained in the case of nickel, and 442 cm.$^{-1}$ in that of palladium. This weak band is possibly a skeletal vibration, as it has been observed for bisdimethylglyoximatonickel(II) at 429 cm.$^{-1}$. The strong absorption band for a metal–oxygen mode, observed in the parent acetylacetone complexes, is missing. Therefore the infrared evidence favours, in this aspect, the structure (II).


(II)


(III)

The diamagnetism also slightly favours structure (II) over (I). Structure (I) involves oxygen as one of the donor atoms to the metal ion and this atom less readily effects spin-pairing.

TABLE 2.

Characteristic infrared frequencies of complexes (III) of nickel and palladium and of bisdimethylglyoximatonickel(II) [Ni(DMG)$_2$].

Compound	3000 cm.$^{-1}$ region	1700—1500 cm.$^{-1}$ region	M–N region	M–O region and skeletal vibrations
$Ni(C_5H_7N_2O_2)_2$ (III)	3236	1681, 1667, 1639, 1629, 1590	537 ± 2 524 ± 2	462 ± 2
$Pd(C_5H_7O_2N_2)_2$ (III)	3247	1678, 1647, 1603	511 ± 2 498 ± 2	442 ± 2
$Ni(DMG)_2$		1575	522 ± 2	429 ± 2

EXPERIMENTAL

Metal acetylacetonates were prepared by methods in the literature.

Bis-(γ-nitroacetylacetonato)copper (II).—Bisacetylacetonatocopper (II) (0·5 g.) in dry benzene was treated with dry dinitrogen tetroxide at room temperature. Reaction occurred

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[9] Powell and Sheppard, *J.*, 1956, 3108.

immediately, and after a few minutes a green precipitate was formed which was filtered off, washed with benzene, recrystallised from chloroform or acetone and dried *in vacuo*. It had m. p. 247° (decomp.) [Found: C, 34·4; H, 3·6; N, 7·4%; *M* (isopiestic in acetone), 334; (ebullioscopic in 1% chloroform solution), 289. $C_{10}H_{12}CuN_2O_8$ requires C, 34·2; H, 3·4; N, 7·9%; *M*, 352]. The *nitro-compound* is soluble in chloroform, acetone, and alcohol and insoluble in water. It is very stable and sublimes under reduced pressure (140°/10^{-2} mm.). It ignites spontaneously in air when heated. In nitrobenzene solution the complex is virtually a non-electrolyte. The compound is paramagnetic ($\chi_g = 4{\cdot}36 \times 10^{-6}$ at 25°), hence $\mu_{eff} = 2{\cdot}0$ B.M.

Bis-(γ-nitroacetylacetonato)nickel(II).—When bisacetylacetonatonickel(II) in benzene was treated similarly, the reaction is not as straightforward; completion is not as easy to detect, since the substance formed does not coagulate so well. Reaction of the acetylacetonate (2·0 g.) in benzene (10 ml.) is complete in 10—15 min. The complex formed being sensitive to moisture, all further operations were carried out in a dry box. The precipitate was filtered off, washed with benzene, and extracted with dry chloroform. The volume of the chloroform was reduced and, on cooling, olive-green leaflets were obtained. The compound decomposes at 110°. It is very hygroscopic and both the analysis and the infrared spectra indicate the presence of water. Experimental evidence does not exclude the possibility that this water is included in the crystal structure (Found: C, 33·3; H, 4·5; N, 6·8. Calc. for $C_{10}H_{12}N_2NiO_8$: C, 34·6; H, 3·5; N, 8·0. Calc. for the monohydrate: C, 32·9; H, 3·9; N, 7·7%). The compound is paramagnetic ($\chi = 12{\cdot}91 \times 10^{-6}$ at 25°), whence $\mu_{eff} = 3{\cdot}3$ B.M.

Bis-(γ-nitroacetylacetonato)platinum(II).—Treated similarly, bisacetylacetonatoplatinum(II) in benzene yielded yellow crystals which were filtered off, washed with benzene, and dried *in vacuo*. The *compound* decomposes at 160° and is insoluble in common solvents (Found: C, 25·5; H, 3·0; N, 6·1. $C_{10}H_{12}N_2O_8Pt$ requires C, 24·8; H, 2·6; N, 5·8%). It is diamagnetic.

Bis-(γ-nitroacetylacetonato)palladium(II).—Bisacetylacetonatopalladium(II) (0·5 g.) was treated with dinitrogen tetroxide in benzene (50 ml.), a brown red precipitate being formed immediately. The precipitate was filtered off, washed with benzene, and dried *in vacuo*. The compound is only slightly soluble in acetone and tetrahydrofuran, and could not be recrystallised or studied in solution. The product of reaction was impure, containing species other than the γ-nitro-complex, as indicated by the analysis (Found: C, 21·3; H, 2·2; N, 9·9. Calc. for $C_{10}H_{12}N_2O_8Pd$: C, 30·4; H, 3·0; N, 7·1%). It decomposes at 185°. The infrared spectrum shows, however, that it contains a complex of the type described above.

Tris-(γ-nitroacetylacetonato)aluminium(III).—Trisacetylacetonatoaluminium(III) (2 g.) in cold sodium-dried benzene (100 ml.) was treated with nitrogen dioxide. The solution became yellow and yellow crystals were deposited. The solution was concentrated, and the product precipitated by addition of light petroleum (b. p. 60—80°). The *compound* was separated from impurities by recrystallisation from benzene–light petroleum and chloroform–light petroleum. It was pale yellow, and virtually a non-conductor in nitromethane and nitrobenzene [Found: C, 39·0; H, 4·0; Al, 6·3; N, 9·3%; *M* (isopiestic in acetone), 430. $C_{15}H_{18}AlN_3O_{12}$ requires C, 39·2; H, 4·0; Al, 5·9; N, 9·2%; *M*, 459].

Bis-(γ-nitroacetylacetonato)aluminium(III).—The same concentrations were used as for the preparation of the tris-(γ-nitroacetylacetonato)aluminium(III); 3 mol. of nitrogen dioxide were added per mol. of trisacetylacetonatoaluminium(III). The benzene solution, which was kept at 0°, became yellow and a precipitate was formed. The solution was set aside for 1 hr., then the excess of nitrogen dioxide was removed by evacuation. The excess of solvent was removed under a vacuum, giving a yellow solid. The pure *compound* was prepared as a pale yellow solid by fractional crystallisation from benzene–light petroleum (Found: C, 44·1; H, 4·9; Al, 6·0; N, 7·3. $C_{15}H_{19}AlN_2O_{10}$ requires C, 43·5; H, 4·6; Al, 6·5; N, 6·8%).

Bis-(γ-deuteroacetylacetonato)copper(II).—Cupric sulphate pentahydrate (0·6 g.) in 99·8% deuterium oxide (5 ml.) was treated with acetylacetone (1 ml.), the latter having previously been shaken with a large excess of deuterium oxide. The precipitate of bisacetylacetonatocopper(II) was filtered off, washed with deuterium oxide, and dried at 105°. The mass-spectroscopical analysis showed that 12·5% of the hydrogen was present as deuterium. This corresponds to a ratio H : D = 7 : 1, indicating that two hydrogen atoms had been exchanged with deuterium to the extent of 88%.

Bis-(γ-chloroacetylacetonato)platinum(II).—Treating bisacetylacetonatoplatinum(II) in benzene with nitrosyl chloride at room temperature gave a yellow precipitate almost immediately. The precipitate was filtered off, washed with benzene, and dried *in vacuo* (Found:

C, 25·9; H, 3·4; Cl, 13·7. $C_{10}H_{12}Cl_2O_4Pt$ requires C, 26·0; H, 2·6; Cl, 15·3%). The *compound* is insoluble in all solvents tried.

Reaction of Bisacetylacetonatonickel(II) *with Nitrite Ions*.—The complex can be prepared under various conditions. The rate of the reaction and the yield vary with the solvent and the pH of the solution.

(*a*) Bisacetylacetonatonickel(II) dihydrate (2 g.) was treated with potassium nitrite (18 g.) in water or alcohol–water (~200 ml.). Ammonium acetate (15 g.) was added as a buffer; the red complex formed was filtered off, washed with water, and dried at 105°. (*b*) Nickel acetate (10 g.) in water or water–alcohol containing ammonium acetate (50 g.) was treated with potassium nitrite (90 g.) in water (30 ml.) and acetylacetone (9 ml.). The pH was ~7. When the mixture was shaken for 1—3 hr., a red complex was gradually precipitated; this was filtered off, washed with water, dried, and recrystallised from benzene. (*c*) Ammonia was bubbled into acetylacetone, yielding the white addition complex $C_5H_8O_2(NH_3)$. The latter was then treated with an aqueous solution of nickel chloride and potassium nitrite containing dilute acid sufficient to give pH ~7; this yielded the red *complex*, insoluble in water and having m. p. 248° (decomp.) [Found: C, 38·4; H, 4·7; N, 17·7; Ni, 18·6%; *M* (isopiestic in 0·3% chloroform solution), 335. $C_{10}H_{14}N_4NiO_4$ requires C, 38·4; H, 4·5; N, 17·9; Ni, 18·8%; *M*, 313], virtually a non-conductor in nitrobenzene and diamagnetic in the powder form (χ_g $-0{\cdot}31 \times 10^{-6}$).

Reaction between Bisacetylacetonatopalladium(II) *and Nitrite Ions*.—(*a*) An aqueous solution of bisacetylacetonatopalladium(II) (0·25 g.) was treated with potassium nitrite (2 g.) in the presence of ammonium acetate (1·5 g.), an orange red precipitate being formed slowly. This was filtered off and washed with water. (*b*) Alternatively, the compound may be prepared from palladous chloride (1 g.) in 2 : 1 water–alcohol (75 ml.) to which ammonium acetate (5 g.) and potassium nitrite (7 g.) were added. When the solution was shaken or stirred for 1—2 hr., the red complex was formed slowly. It was filtered off, washed with water, dried *in vacuo*, and recrystallised with difficulty from chloroform, in which it is only slightly soluble. The *compound* decomposes without melting above 220° (Found: C, 33·0; H, 4·1; N, 15·7. $C_{10}H_{14}N_4O_4Pd$ requires C, 33·3; H, 3·9; N, 15·5%) and is only slightly soluble in tetrahydrofuran, insoluble in water, and diamagnetic (χ_g $-0{\cdot}15 \times 10^{-6}$).

Infrared Spectra.—Spectra in the region 5000—500 cm.$^{-1}$ were recorded with a Grubb–Parsons double-beam infrared spectrophotometer, equipped with a S3A monochromator and calcium fluoride (5000—2000 cm.$^{-1}$) and potassium bromide (2000—500 cm.$^{-1}$) prism, combined with a grating. The samples were examined in the solid state in Nujol or hexachlorobutadiene mulls or in chloroform and acetone solutions. Spectra in the region 600—400 cm.$^{-1}$ were recorded with a Unicam double-beam S.P. 100 infrared spectrophotometer, equipped with a potassium bromide prism.

One of us (C. D.) is grateful to the Rudjer Boskovic Institute, Zagreb, Yugoslavia, for a grant. We thank Mr. R. Long for permission to publish the work dealing with the tri- and di-substituted nitro-complexes of trisacetylacetonatoaluminium(III).

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[*Received, May* 15*th*, 1962.]