17 kK remains essentially unchanged at all temperatures investigated. The molar absorptivity, however, decreases to about 20% of its value at room temperature. This reversible variation in the strength of the absorption is readily observed during the preparation of the glasses as they reach their deepest coloration only after complete cooling. At present no explanation for this change in intensity can be given. A similar effect is observed in the emission spectra which were measured between 20 and 300°. In this case, however, a strong shift toward higher energies from 17 to 18.5 kK is observed leading to a change in the color of the fluorescent emission from orange to greenish yellow at 300°. Together with the excitation spectrum at 23.5 kK at 20°, the observed transitions may be explained in the following simplified way. The absorption at 17 kK is due to the allowed transition from the $^2\Pi_g$ ground state of the S_2^- ion to its first excited state $^2\Pi_u$. The weak band in the S_2^- spectrum at around 24 kK, as observed in organic solution and as the excitation band in the borate glasses, then is attributed to a parity-forbidden transition from $^2\Pi_g$ to some unspecified state ^2X_g. From this state the excited molecule may return to $^2\Pi_g$ *via* a radiationless transition to $^2\Pi_u$. The remainder of the energy then is emitted during the transition from $^2\Pi_u$ to the ground state. Similar emission and excitation spectra have been reported[14] for sulfur-doped alkali halide crystals containing the S_2^- ion, thus proving the presence of this ion in sulfur-doped borate glasses and in ultramarine which also exhibits an orange emission with a maximum at 17.2 kK on exposure to long-wavelength uv radiation.

Whereas the spectroscopic data presented thus far are in agreement with the assumption of the sole formation of the S_2^- ion in polysulfide-containing melts at elevated temperatures, esr spectra indicate the presence of another radical species in significant amounts. As outlined in a previous study,[9] the S_2^- cannot be expected to exhibit any sharp detectable esr absorption except for very low temperatures. The relatively sharp three-line esr absorption with $g_1 = 2.050$, $g_2 = 2.031$, and $g_3 = 2.003$ at 90°K readily observed in blue sulfur-doped borate glasses,[15] therefore, is tentatively ascribed to the S_3^- ion. The presence of this ion was unumbiguously established in sulfur-doped alkali halide crystals;[16] it exhibited an esr absorption with $g_x = 2.049$, $g_y = 2.035$, and $g_z = 2.001$. The presence of S_3^- in addition to the S_2^- ion in ultramarine is indicated by the appearance[17] of an ir absorption at 580 cm^{-1} and the characteristic three-line esr absorption in "dilute" ultramarine.[18,19] By comparison with a DPPH standard[9] the absolute concentration of S_3^- ions in sulfur-doped borate glasses was found to vary between 10 and 15% of that of the S_2^- ion as determined by its absorbance at 17 kK. No indication of its presence, however, could be detected in the absorption spectra of borate glasses exhibiting a strong esr absorption.

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[14] J. Rolfe, *J. Chem. Phys.*, **49**, 4193 (1968).

[15] Y. Matsunaga, *Can. J. Chem.*, **38**, 310 (1960).

[16] J. Schneider, B. Dischler, and A. Räuber, *Phys. Status Solidi*, **13**, 141 (1966).

[17] U. Hofmann, E. Herzenstiel, E. Schönemann, and K. H. Schwarz, *Z. Anorg. Allg. Chem.*, **367**, 119 (1969).

[18] G. Yamaguchi and Y. Kubo, *Bull. Chem. Soc. Jap.*, **41**, 2641 (1968).

[19] R. Böttcher, S. Wartewig, W. Windsch, and A. Zschunke, *Z. Naturforsch. A*, **23**, 1766 (1968).

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Cyclic Peroxo Complexes of Platinum(II) with α-Diketones. A Novel Preparation of "Mixed" Carboxylates

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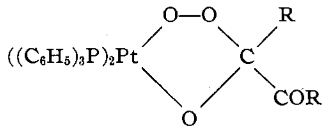
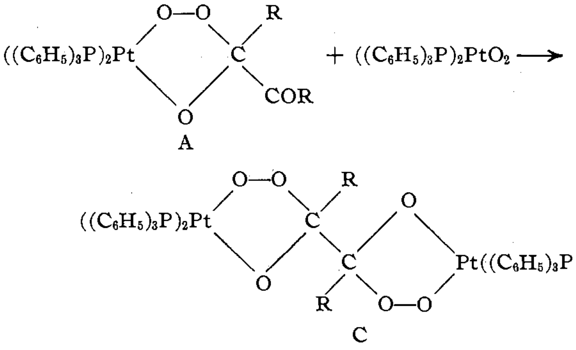
We have previously shown[1-3] that peroxobis(triphenylphosphine)platinum(II) will react with compounds containing a single carbonyl group to give adducts in which the metal and the peroxo group form part of a five-membered ring. We now report that a similar reaction will take place with α-diketones to give a product in which just one of the carbonyl groups is incorporated into the cyclic part of the structure, the other remaining "free." The initial adducts will then react with 1 further mol of $((C_6H_5)_3P)_2PtO_2$ to give a dinuclear species in which both carbonyl groups are coordinated

RCOCOR + $((C_6H_5)_3P)_2PtO_2 \longrightarrow$

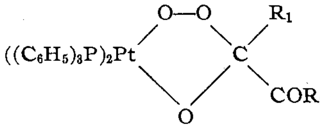


(1)

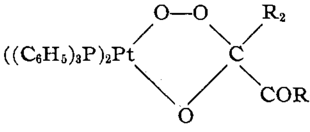


(2)

Adducts have been prepared with 2,3-butanedione ($CH_3COCOCH_3$), 2,3-pentanedione ($C_2H_5COCOCH_3$), 1-phenyl-1,2-propanedione ($C_6H_5COCOCH_3$), *p*-methoxy-1-phenyl-1,2-propanedione ($CH_3OC_6H_4COCOCH_3$), and benzil ($C_6H_5COCOC_6H_5$). With glyoxal, only a diformate could be isolated (see later). The initial products are all pale green and show the expected carbonyl stretching band due to the uncomplexed C=O at about 1700 cm^{-1} in the ir spectrum. When an unsymmetrical diketone is used, there is the possibility of forming two isomers of the initial adduct



A



B

and, in general, a mixture was obtained. We have

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[1] P. J. Hayward, D. M. Blake, C. J. Nyman, and G. Wilkinson, *Chem. Commun.*, 987 (1969).

[2] P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, **92**, 5873 (1970).

[3] P. J. Hayward and C. J. Nyman, *ibid.*, **93**, 617 (1971).

TABLE I

INFRARED AND NMR SPECTRA OF THE ADDUCTS[a]

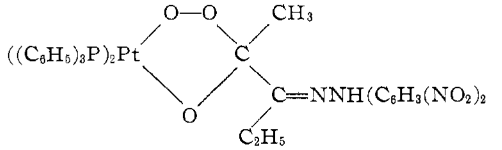
Compound	ν(C=O), cm^{-1}	^{1}H nmr spectra, ppm downfield from TMS in CH_2Cl_2 soln		
		Phenyl	R_1	R_2
$R_1 = CH_3$, $R_2 = CH_3$				
Ligand	1710 vs	. . .	2.27	2.27
Adduct A	1710 vs	7.26 (30)	1.43 (3)	2.29 (3)
Dinucl adduct C	. . .	7.25 (60)	1.42 (3)	1.42 (3)
Carboxylate D	1625 vs	7.29 (30)	1.37 (3)	1.37 (3)
$R_1 = C_2H_5$, $R_2 = CH_3$				
Ligand			2.75 q (2), 1.07 t (3)	2.28 (3)
Adduct A (30%)	1710 vs	7.25 (30)	1.65 u (2) 0.60 t (3)	2.22 (3)
Adduct B (70%)	1710 vs	7.25	2.70 q 1.00 t	1.37
Carboxylate D	1625 vs	7.39 (30)	1.57 pq (2), 0.50 t (3)	1.27 (3)
$R_1 = C_6H_5$, $R_2 = CH_3$				
Ligand			7.5–8.0 (5)	2.43 (3)
Adduct A (80%)	1715 vs	7.13 (30)	7.13 (5)	2.20 (3)
Adduct B (20%)	1715 vs	7.13	7.13	1.64
Carboxylate D	1635 vs	7.22 (30)	7.22 (5)	1.27 (3)
$R_1 = p$-$CH_3OC_6H_4$, $R_2 = CH_3$				
Ligand			7.80 d (2), 6.80 (2), 3.80 (3)	2.43 (3)
Adduct A (70%)	1710 s	7.28 (30)	7.28 (4) 3.67 (3)	2.12 (3)
Adduct B (30%)	1710 s	7.28	7.28 3.76	1.60
Carboxylate D	1600 vs	7.32 (30)	7.32 (4), 3.60 (3)	1.20 (3)
$R_1 = C_6H_5$, $R_2 = C_6H_5$				
Ligand	1670 vs			
Adduct A	1685 vs			
Dinucl adduct C	. . .			
Carboxylate C	1630 1615 vs			
$R_1 = CH_2CH_2COCH_3$, $R_2 = CH_3$				
Ligand			2.68 (4), 2.15 (3)	2.15 (3)
Adduct A	1705 vs	7.23 (30)	2.25 (4), 1.97 (3)	1.53 (3)

[a] Abbreviations: d, doublet; t, triplet; q, quartet; u, unresolved; p, partly resolved. Figures in parentheses are relative intensities.

previously shown[2] that there is an upfield shift in the magnetic resonance spectra of the protons in the alkyl groups directly attached to the cyclic carbon, whereas the spectra of these protons in the alkyl groups attached to the carbonyl carbon were little changed. The appearance of the signals to high field enabled us both to detect the new compounds and to estimate the composition of the isomeric mixture (by comparison of peak areas). See Table I for the ir and nmr spectra of the adducts.

The main factor governing the distribution in the isomeric mixture is not obvious. When $R_1 = C_2H_5$ (R_2 was always CH_3 in the present study), the ratio A:B = 30:70 (±5%) and when $R_1 = C_6H_5$, A:B = 80:20 (±5%). With p-$(CH_3O)C_6H_4COCOCH_3$, the ratio A:B = 70:30 (±5%). These results suggest that a steric effect is in operation and yet we cannot discount the electronic contribution previously indicated.[4]

As previously mentioned, the 1:1 adducts (A, B) show the expected bands, arising from the carbonyl stretch, at about 1700 cm^{-1}. The properties of this carbonyl group appear to be little affected by its proximity to the adjacent cyclic structure and, while there is a slight reduction in reactivity, the 2,4-dinitrophenylhydrazone derivative can be isolated. For example, with the 1:1 adduct of 2,3-pentanedione



is isolated. It was determined that ν(C=N) = 1615 cm^{-1}.

The 1:1 adducts with α-diketones undergo a novel rearrangement to give, eventually, a dicarboxylate, D. In the instance of the unsymmetrical diketones, 100% of the "mixed" carboxylate rather than a mixture of the two separate species was obtained. For example, from $((C_6H_5)_3P)_2PtO_2 \cdot C_6H_5COCOCH_3$ the compound $((C_6H_5)_3P)_2Pt(OCOC_6H_5)(OCOCH_3)$ was obtained whose nmr spectrum showed two distinct proton resonances. The identity of the "mixed" carboxylate was readily established by comparing the positions of these signals with those of the diacetato and dibenzoato complexes. This, plus the fact that the rearrangement proceeds slowly in the solid state, suggests that the change is intramolecular. The rate of reaction appears to be independent of solvent and the presence of oxygen but is catalyzed by light. The decomposition may be followed by observing changes in the ir and nmr solution spectra. For example, with $((C_6H_5)_3P)_2PtO_2 \cdot CH_3COCOCH_3$, two intermediates may be detected. The structures of the intermediates, which unfortunately could not be isolated, are as yet unknown, but the nmr spectrum shows that the two methyl groups remain nonequivalent until the final step. Similar changes may be noted during rearrangement of the other α-diketone adducts. In general, the bulkier the substituents on the diketone, the less stable the adducts and the more rapid the rearrangement. An exception to this, however, is the reaction of glyoxal. Here, rearrangement was so rapid that no peroxy adduct at all could be isolated.

No rearrangement occurs in the 2,5-hexanedione adducts nor in any α-diketone complexes in which the second carbonyl group is not "free." For example, the

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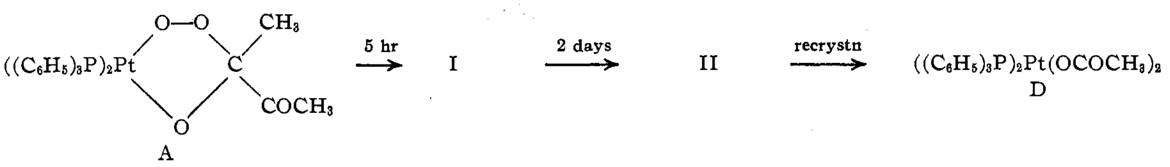
(4) R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Commun.*, 1498 (1968).



	A	I	II	D
Ir C=O	1710 vs	1825 m 1620, 1600 vs	1715 vs 1620, 1600 vs	1625 vs
Nmr Alkyl ^{1}H	2.29 (3) 1.43 (3)	2.19 (3) 1.32 (3)	2.07 (3) 1.32 (3)	1.37 (b)

2,4-dinitrophenylhydrazine derivative of $((C_6H_5)_3P)_2PtO_2 \cdot C_2H_5COCOCH_3$ and the dinuclear adducts are quite stable.

Experimental Section

Materials.—The diketones, with the exception of *p*-methoxy-1-phenyl-1,2-propanedione were Eastman Organic Chemicals. The latter was prepared by oxidation of anisylacetone (ROC/RIC Co., Sun Valley, Calif.) with selenium dioxide using an adaptation of the method of Riley and Gray.[5] The required product was distilled under reduced pressure at 77° and was recovered as bright yellow-green crystals, mp 42–44°. The purity of all the diketones was checked by nmr, and in most cases, no further purification was considered necessary. The complex $((C_6H_5)_3P)_2PtO_2$ was prepared as previously described.[2]

Preparation of the Complexes.—Monoadducts were prepared as previously described.[2] The dinuclear compounds were prepared by warming gently, under an atmosphere of nitrogen, a 1:1 mixture of the mononuclear adduct and $((C_6H_5)_3P)_2PtO_2$ in the minimum of CH_2Cl_2 until the orange color of the solution faded to a pale yellow (*ca.* 5 min). Ether was added to precipitate the complexes, the purity of which could readily be checked by the disappearance of the ir bands due to starting materials at 820 and 1700 cm^{-1}. Excessive or prolonged heating caused decomposition of the complexes.

Dicarboxylates formed on allowing the mononuclear adducts to stand for periods varying between a few hours and several days (see discussion in text) in CH_2Cl_2 solution. Some unidentified dark organic material also formed but this could be minimized if the solution was kept under an inert atmosphere (N_2 or Ar). The 2,4-dinitrophenylhydrazine derivative of $((C_6H_5)_3P)_2PtO_2 \cdot C_2H_5COCOCH_3$ was prepared by adding, dropwise, a hot saturated ethanolic solution of the reagent to a solution of the complex in the minimum CH_2Cl_2. The orange derivative precipitated almost immediately, was filtered off, washed with ether, and dried *in vacuo*. See Table II for analytical results.

Physical Measurements.—Proton nmr spectra were obtained on a Varian A-60 spectrometer and the ir spectra on a Perkin-Elmer 700 (correct to ±5 cm^{-1}).

TABLE II

ANALYTICAL RESULTS

Compound	Mp, °C	% C		% H		% P	
		Calcd	Found	Calcd	Found	Calcd	Found
$R_1 = CH_3$, $R_2 = CH_3$							
Adduct A	106–108 dec	57.3	57.3	4.3	4.3	7.4	7.1
Dinucl adduct C[a]	111–115 dec	57.4	56.9	4.2	4.0	7.8	7.5
Carboxylate D	203–205	57.3	56.9	4.3	4.4	7.4	6.9
$R_1 = C_2H_5$, $R_2 = CH_3$							
Adducts A and B	138–140 dec	57.8	57.5	4.5	4.6	7.2	7.0
Carboxylate D	205–210	57.8	57.3	4.5	4.4	7.2	7.2
2,4-DNPH deriv of A and B[b]	275 dec	54.7	54.1	4.1	3.9	6.0	6.0
$R_1 = C_6H_5$, $R_2 = CH_3$							
Adducts A and B	105–108 dec	60.0	59.7	4.3	4.4	6.9	7.1
Carboxylate D	175 dec	60.0	59.7	4.3	4.3	6.9	7.0
$R_1 = p\text{-}CH_3OC_6H_4$, $R_2 = CH_3$							
Adducts A and B	110–125 dec	59.4	58.9	4.3	4.4	6.7	6.4
Carboxylate D	145–150 dec	59.4	58.6	4.3	4.0	6.7	6.1
$R_1 = C_6H_5$, $R_2 = C_6H_5$							
Adduct A	108–112 dec	62.4	61.3	4.2	4.2	6.4	6.0
Dinucl adduct C		60.3	58.9	4.1	3.9	7.2	6.2
Carboxylate D	206–208	62.4	61.6	4.2	4.1	6.4	6.1
$R_1 = CH_3COCH_2CH_2$, $R_2 = CH_3$							
Adduct A	131–133 dec	58.3	58.4	4.6	4.5	7.2	7.3
Dinucl adduct C[c]	122–126 dec	57.9	57.6	4.4	4.1	7.6	7.5

[a] Molecular weight: calcd, 1589; found, 1387. [b] Nitrogen analysis: calcd, 5.4; found, 5.2. [c] Molecular weight: calcd, 1617; found, 1035. There is considerable dissociation in solution.

Acknowledgment.—The authors wish to thank Dr. R. A. Bartsch for helpful discussions.

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[5] H. A. Riley and A. R. Gray in "Organic Syntheses," A. H. Blatt, Ed., Collect. Vol. 2, Wiley, New York, N. Y., 1943, p 509.

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The Electron-Impact Ionization Potentials of Successively Substituted Acetylacetonates of Rhodium(III)

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We have continued our examination of ionization potentials measured with a mass spectrometer for series of metal acetylacetonates where each ring has a dif-

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[2] NSF Trainee, 1966–1970.