BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49 (10), 2877—2878 (1976)

Some New β-Diketone Complexes of Ruthenium(III) with Triphenylphosphine and Triphenylarsine

K. NATARAJAN and Umesh AGARWALA

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, U.P., India

(Received April 7, 1976)

Synopsis. The syntheses of some new β-diketone complexes of Ru(III) with triphenylphosphine and triphenylarsine have been described. Their spectral (IR and visible) and magnetic properties have been reported. Some of them show unusual magnetic moment.

Mixed complexes of ruthenium(II) with triphenylphosphine and β-diketones have been reported in the literature,1) but no work has so far been done on similar complexes of ruthenium(III).

In this communication, we report the preparations of the ruthenium(III) complexes of the type [RuX_2L_2(bdk)] (X=Cl, Br; L=PPh_3, $AsPh_3$; bdk=acetylacetonate, dibenzoylmethanate, benzoylacetonate) starting from [$RuCl_3(AsPh_3)_3$],2) [$RuBr_3(AsPh_3)_3$],3) [$RuCl_3(PPh_3)_3$],4) and [$RuBr_3(PPh_3)_2$(MeOH)].5) Their spectral and magnetic properties have also been studied.

The general procedure to prepare these complexes is as follows:

A solution of 0.4 g of [RuX_3L_3] or [RuX_3L_2(MeOH)] in 20 ml of benzene or dichloromethane was mixed with another solution of β-diketone (0.2 g) in 5 ml of ethyl alcohol. It was heated under reflux for 3—5 h whereby the desired complex was separated out on concentrating the refluxing solution. The colour in the case of chloro complexes was green while that of bromo ones, brown. All the compounds were recrystallized from dichloromethane–methanol mixture.

Magnetic susceptibilities of the complexes were determined with a Gouy balance. The electronic spectra of the complexes were recorded in chloroform solution with a Cary-14 recording spectrophotometer in the range of 1000—300 nm. The infrared spectra of the complexes were taken with the help of a Perkin-Elmer 521 grating infrared spectrophotometer in the range of 4000—300 cm^{-1} using KBr pellets of the samples. The major IR bands are given in Table 1.

TABLE 1.

Sl. No.	Complex	Mp °C	Magnetic moment B.M.	IR bands cm^{-1}
1	$RuCl_2(acac)(AsPh_3)_2$	267	2.54	1530, 1565
2	$RuCl_2(dbm)(AsPh_3)_2$	281	2.53	1540, 1610
3	$RuCl_2(ba)(AsPh_3)_2$	255	2.10	1530, 1570, 1610
4	$RuCl_2(acac)(PPh_3)_2$	215	2.00	1530, 1570
5	$RuCl_2(dbm)(PPh_3)_2$	230	2.71	1525, 1540, 1600
6	$RuCl_2(ba)(PPh_3)_2$	214	2.31	1540, 1560
7	$RuBr_2(acac)(AsPh_3)_2$	290	2.03	1530, 1570
8	$RuBr_2(dbm)(AsPh_3)_2$	267	2.07	1530, 1570
9	$RuBr_2(ba)(AsPh_3)_2$	231—233	2.02	1530, 1570, 1605
10	$RuBr_2(acac)(PPh_3)_2$	224	1.80	1545, 1575
11	$RuBr_2(dbm)(PPh_3)_2$	222	2.00	1535, 1550, 1610
12	$RuBr_2(ba)(PPh_3)_2$	206	1.91	1535, 1560, 1600

acac=acetylacetonate; dbm=dibenzoylmethanate; ba=benzoylacetonate.

The analytical data of carbon, hydrogen, ruthenium and halide ion of the complexes confirm the general formula [RuX_2L_2(bdk)].

The IR spectra of the complexes showed all the bands due to triphenylphosphine or triphenylarsine. Besides these, two or three bands were also present in the region 1525—1610 cm^{-1}. These may be assigned to the characteristic bands of the coordinated β-diketones arising due to the normal coordinates having contributions from ν(C=O) and ν(C=C).6,7) The molecular weight determination in bromoform solution of the complexes confirm monomeric structure for all the compounds.

The electronic spectra of all the complexes in chloroform solution showed two to three bands in the region 600—350 nm. The bands are very much characteristic of the octahedral surrounding of the ligand molecules around ruthenium(III) ions.8–10) Generally in the visible region ruthenium(III) ion show charge transfer bands around 400 nm.11,12) It is also clear by the shift in the positions of both the bands in the bromo complexes towards lower wavelength side because of the greater reducing power of Br than Cl.12)

The values of the magnetic moments were a little abnormal (see Table 1). Since ruthenium(III) belongs to d^5 system, having one unpaired electron, it should normally show a value of the magnetic moment around 2.00 B. M. In some of the cases of β-diketone derivatives of ruthenium(III), the values of magnetic moment are found to be in the range of 2.3—2.7 B. M. This high value can not be explained by the presence of one unpaired electron and hence a spin-free system must be invoked.13) In order to explain this, further studies on low temperature magnetic measurements and ESR are under progress. Preliminary ESR studies showed the presence of two lines, indicating distorted octahedral nature of the complexes.14)

References

1) J. D. Gilbert and G. Wilkinson, *J. Chem. Soc., A*, **1969**, 1749.

2) R. K. Poddar, I. P. Khullar, and U. Agarwala, *Inorg. Nucl. Chem. Lett.*, **10**, 221 (1974).

3) K. Natarajan, R. K. Poddar, and U. Agarwala, *J. Inorg. Nucl. Chem.*, in press.

4) J. Chatt, G. J. Leigh, D. M. P. Mingos, and R. J. Paske, *J. Chem. Soc., A*, **1968**, 2636.

5) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 945 (1966).

6) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, New York, N. Y.

(1964).

7) David M. Adams, "Metal-Ligand and Related Vibrations," New York, St. Martins Press (1968).

8) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw Hill Book Co., New York (1962).

9) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier Publishing Co., Amsterdam, London, New York (1968).

10) K. Natarajan, R. K. Poddar, and U. Agarwala, *J. Inorg. Nucl. Chem.*, **38**, 249 (1976).

11) A. E. Martell, "Coordination Chemistry," Vol. 1, Van Nostrand Reinhold, New York, N. Y. (1971).

12) B. N. Figgis, "Introduction to Ligand Field Theory," Interscience Publishers, New York, N. Y. (1966).

13) T. A. Stephenson and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **28**, 2285 (1966).

14) J. Chatt, G. J. Leigh, and D.M.P. Mingos, *J. Chem. Soc., A*, **1969**, 1674.