The O–O Bond Length in Oxygen Adducts of Iridium and Rhodium Complexes

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Summary The O–O bond length in dioxygen complexes of Rh and Ir compounds lies in the range 1·45—1·50 Å; the long bond of 1·625 Å reported for $[IrO_2(dppe)_2]^+$† is an artefact caused by crystal decomposition.

FROM results of *X*-ray determinations[1–3] on rhodium and iridium dioxygen complexes, inferences[3] were drawn relating the metal and ligand to variations in M–O and O–O bond lengths, and to the 'uptake properties' of the complex towards oxygen. However, the recent structure determination[4] of $[IrO_2ClCO(PEtPh_2)_2]$ showed an anomaly; although the dioxygen ligand is reversibly taken up, the O–O length of 1·46 Å falls close to the value supposedly typical of irreversible oxygen uptake. Thus, as a further test of these trends[3] we undertook to determine the crystal structures of a series of dioxygen salts, $[MO_2(L_2)_2]X$ [M = Ir or Rh, L = PMe_2Ph, X = BPh_4 (I and II); M = Rh, L = $AsMe_2Ph$, X = ClO_4 (III)], as changing L_2 from dppe† to $(PMe_2Ph)_2$ or $(AsMe_2Ph)_2$ should cause an increase in O–O bond lengths (*cf.* 1·46 and 1·625 Å for $[MO_2(dppe)_2]PF_6$,† M = Rh and Ir respectively). The O–O values obtained from our determinations were in the range 1·43—1·49 Å which was unexpected as theory[3] predicted that the bonds should be longer than 1·6 Å. At this stage, the crystal structure of

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† dppe = $Ph_2PCH_2CH_2PPh_2$, dppen = $Ph_2PCH{:}CHPPh_2$, and dppm = $Ph_2PCH_2PPh_2$.

the cation [CoO$_2$(dppen)$_2$]$^+$† (irreversible oxygen uptake) was reported[5] with an O–O length of 1·46 Å and comments on the anomalous O–O bond length of 1·45 Å in the stable [Pt(PPh$_3$)$_2$O$_2$] complex were recorded.[6] The immediate conclusion was that the O–O bond length was essentially independent of the metal involved, and that it could not be correlated with the rate or degree of oxygen uptake. To measure the effect of changing the geometry of the ligand and as a check on internal consistency, the compounds [IrO$_2$(dppm)$_2$]X† [X = ClO$_4$ (IV) or PF$_6$ (V)] were prepared and their structures determined. As a final check on the results, [IrO$_2$(dppe)$_2$]PF$_6$ (VI)† was also prepared and its structure redetermined.[7] There were large differences between ours and previous[3] co-ordinates of the iridium and phosphorus atoms probably because the earlier results were affected by systematic errors in the intensity data associated with crystal decomposition. A detailed study[7] of the decomposition was therefore carried out, which confirmed our hypothesis. Results (including corrections for absorption and anomalous scattering) for the compounds are summarised in the Table. There are no obvious trends in O–O bond lengths (mean value 1·48 Å), in M–O lengths (mean value 2·04 Å), or in M–P lengths [mean values 2·37 Å (*ax.*) and 2·32 Å (*eq.*)].

TABLE

	Compound	O–O σ(0·01—0·03)	M–O (0·01—0·02)	M–P/As (0·005—0·01Å)			Observed data
				ax.	*eq.*	*R*	
(I)	[IrO$_2$(PMe$_2$Ph)$_4$]BPh$_4$	1·49	2·05, 2·04	2·40 2·39	2·31 2·33	0·05	3312
(II)	[RhO$_2$(PMe$_2$Ph)$_4$]BPh$_4$	1·43	2·04, 2·03	2·39 2·39	2·33 2·32	0·08	3861
(III)	[RhO$_2$(AsMe$_2$Ph)$_4$]ClO$_4$	1·46	2·03, 2·03	2·47 2·44	2·43 2·42	0·06	4404
(IV)	[IrO$_2$(dppm)$_2$]ClO$_4$†	1·49	2·06, 2·05	2·37 2·34	2·32 2·31	0·05	3495
(V)	[IrO$_2$(dppm)$_2$]PF$_6$†	1·45	2·00, 2·01	2·37 2·36	2·30 2·31	0·06	3371
(VI)	[IrO$_2$(dppe)$_2$]PF$_6$†	1·52	2·05, 2·05	2·36 2·35	2·31 2·34	0·04	4007

No irregularity is observed for the Ir–P bond lengths in [IrO$_2$ (dppe)$_2$]$^+$,† which is not unexpected as the bonds are chemically equivalent.[8] It is thus evident that the precision previously reported for the bond lengths in the cation [IrO$_2$(dppe)$_2$]$^+$† is over-optimistic and that the estimated standard deviations should probably be at least doubled (in keeping with observations by Hamilton, *et al.*[9–11]). We therefore conclude that (i) the long O–O bond of 1·625 Å and the unusual Ir–P lengths of 2·283 and 2·452 Å previously reported[3] are caused by systematic changes in reflection intensities that accompany crystal decomposition.[7] It is also important to note that the reported value[1] of 1·30 Å for the O–O bond length in [IrO$_2$ClCO(PPh$_3$)$_2$] too may be an artefact caused by the disorder in the crystal, because the O–O distance in the closely related compound [IrO$_2$ClCO(PEtPh$_2$)$_2$] is 1·46 Å. (ii) The true O–O bond length in this class[12,13] of complex probably lies in the range 1·45—1·50 Å, and hence has peroxide (1·49 Å) character. (iii) The widely accepted[14] deductions previously drawn[3] about the bonding between the dioxygen moiety and the metal atom are not tenable. These results indicate that from a chemical standpoint, several concurring crystallographic studies are required to substantiate a bonding model, as any single experiment may give an erroneous result. (iv) No crystal structure determination to date has shown a correlation to exist between O–O bond length and oxygen lability.

(*Received*, 22*nd April* 1975; *Com.* 462.)

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