

C O N T E N T S

<u>Chapter</u>	<u>Title</u>	<u>Page</u>
I	<u>X-RAY SPECTRA</u>	-
1.1	Introduction	1
1.2	X-ray emission spectrum	1
1.2.a	Characteristic spectrum	1
1.2.b	Continuous spectrum	3
1.3	Mechanism of X-ray emission and absorption	5
1.4	Shape and position of the absorption discontinuity	8
1.5	Fine structure in X-ray absorption spectrum	9
1.6	Chemical effects	9
1.6.a	Bonding effects	11
1.7	Special features of X-ray absorption spectroscopy	11
1.8	Orientation of the work	12
	REFERENCES	14
II	<u>EXPERIMENTAL TECHNIQUE</u>	-
2.1	Introduction	17
2.2	X-ray source	17
2.2.a	Power supply unit	18
2.2.b	X-ray tube	19
2.2.c	Cooling system	19
2.3	Spectral region	21
2.4	Spectrograph	21

Contents (contd... 2)

<u>Chapter</u>	<u>Title</u>	<u>Page</u>
2.4.a	Crystal holder	- 23
2.4.b	Film holder	- 23
2.4.c	Arm and film holder carriage	- 25
2.5	Dispersing medium	- 25
2.5.a	Selection of the crystal	- 25
2.5.b	Mounting of the crystal	- 26
2.6	Principle and setting of the spectrograph	- 26
2.7	Optimum conditions for obtaining good spectra-	30
2.7.a	High tension	- 30
2.7.b	Thickness of the absorber	- 31
2.7.c	Placement of the absorber	- 32
2.7.d	Exposure and photographic processing	- 32
2.8	Microphotometry and measurements	- 33
2.9	Dispersion and accuracy of results	- 35
2.10	Preparation of complexes	- 36
2.10.a	Preparation of trans-dinitro-bis- ethylenediamine cobalt(III) nitrate	- 36
2.10.b	Preparation of cis-dinitro-bis- ethylenediamine cobalt(III) nitrate	- 37
2.10.c	Preparation of trans-dichlorobis- ethylenediamine cobalt(III) chloride	- 38
	REFERENCES	- 39

Contents (contd... 3)

<u>Chapter</u>	<u>Title</u>	<u>Page</u>
III	<u>THEORIES OF CO-ORDINATE BOND</u>	-
3.1	Introduction	41
3.2	Hybrid orbitals	45
3.2.a	Localized and delocalized orbitals	47
3.3	Basic concepts in Co-ordination chemistry	47
3.4	Valence bond theory	50
3.4.a	Defects in VB model	52
3.5.a	Electrostatic theory and crystal field theory	53
3.5.b	Crystal field theory	55
3.5.c	Distribution of electrons in the 'd' orbitals	56
3.5.d	Factors affecting the magnitude of $10Dq$	60
3.6	Molecular orbital theory and Ligand field theory	61
	REFERENCES	67
IV	<u>X-RAY ABSORPTION SPECTROSCOPIC STUDY</u>	-
4.1	Introductory discussion	69
4.2	Cobalt complexes	74
4.2.a	Cobaltic complexes	74
4.2.b	Cobaltic amines	74
4.3	Octahedral complexes	75
4.4	Cobalt K-edge in pure cobalt metal	76
4.5	Shape, structure and chemical shift of Co-K edge in Co(III) complexes	77
4.5.a	Cobalt complexes of the form $\text{trans}[\text{Co}(\text{AA})_2(\text{NO}_2)_2]\text{NO}_3$	83

Contents (contd... 4)

<u>Chapter</u>	<u>Title</u>	<u>Page</u>
4.5.b	Cobalt complexes of the form $\text{trans}[\text{Co}(\text{AA})_2(\text{B})_2]^{+1}$	- 87
4.5.c	Cis-trans isomers of cobalt complexes of the form $[\text{Co}(\text{AA})_2(\text{NO}_2)_2]^{+1}$	- 90
4.6	EXAFS of cobalt K-edge in Co(III) complexes	- 90
4.6.a	Low energy absorption	- 97
4.6.b	MO energy level diagram for octahedral complexes of Co(III)	- 98
4.6.c	Diagnosis of cis-trans isomers	- 100
4.6.d	Application of Levy's method	- 101
4.6.e	Application of Lytle's method	- 103
4.6.f	Application of Lytle, Sayers and Stern's (LSS) theory	- 112
	REFERENCES	- 120
V	<u>SUMMARY AND CONCLUSIONS</u>	- 128
	REFERENCES	- 133
	PUBLICATIONS	- 134
	ACKNOWLEDGEMENTS	- 135

*