Asian Journal of Chemistry Vol. 15, No. (3 & 4) (2003), 1828–1830

NOTE

Antifungal Activity of Some Transition Metal Ferrocyanides

CHARU ARORA and R.D. KAUSHIK*

Department of Chemistry, Gurukul Kangri University, Haridwar-249 404, India

Ferrocyanides of Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) have been synthesized by known methods and their hitherto unstudied fungicidal potential tested against *Mycogone perniciosa* and *Rhizoctonia solani*—the mushroom and paddy fungal pathogens respectively.

Key Words: Antifungal activity, Transition metal ferrocyanides.

Transition metal ferrocyanides are well known for their ion exchange[1–5], catalytic and adsorption properties[6–8]. There are few reports on antitumor activity of some platinum complexes[9]. Studies on their medicinal and agricultural properties have not been reported yet. These metals are present in traces in the soil and Zn, Cu etc. are required for crops like rice, pulses, etc. Keeping these facts in view, the present investigations have been undertaken.

Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) ferrocyanides were prepared following the Kourim's method[10]. Potassium ferrocyanide (167 mL of 0.1 M) and 500 mL of 0.1 M solution of metal salt were mixed with constant stirring at room temperature, heated on a water bath at 80°C for 3–4 h and allowed to stand at ambient temperature for 24 h to get precipitate that was filtered under vacuum and washed thoroughly with doubly distilled water, dried in an oven at 60°C and ground and sieved to 100 mm size. A little excess of metal salt solution, markedly improved the coagulation of the precipitate. The metal ferrocyanides (MF) were characterized by using elemental analysis (carried on Carlo Erba 1108 CHN analyzer), IR spectra (KBr disc on Bio-red FTIR spectrophotometer) and magnetic susceptibility measurements. Metals were estimated on Perkin-Elmer 3100 atomic absorption spectrometer. All metal-ferrocyanides showed a broad band in the range 3750–3400 cm^{-1} (due to interstitial water), at 1631–1600 cm^{-1} (HOH bending), sharp peak at 2080 ± 10 cm^{-1} (CN stretching) and 691–590 cm^{-1} (Fe—C stretching). TGA and DTA studies revealed the broad endothermic water loss step between 18–170°C confirming the presence of lattice water not coordinated to Fe(II). Mass loss was equivalent to 2–7 moles of water except in case of Cd(II) ferrocyanide. Observed magnetic moments were found to be in good agreement with the calculated values. The molecular formulae established on the basis of these studies[4, 12] are $Mn_2[Fe(CN)_6]\cdot 3H_2O$, $Ni_2[Fe(CN)_6]\cdot 5H_2O$,

$Co_2[Fe(CN)_6]\cdot 2H_2O$, $Cu_2[Fe(CN)_6]\cdot 7H_2O$, $Zn_2[Fe(CN)_6]\cdot 3H_2O$ and $Cd_2[Fe(CN)_6]$.

Fungal cultures of *Mycogone perniciosa* and *Rhizoctonia solani*, the well known fungal pathogens causing the wet bubble of *A. bisporus* (mushroom) and blast disease in paddy respectively, were procured from Department of Plant Pathology, G.B. Pant University of Agriculture and Technology, Pantnagar (India). They were cultured in our laboratories in petri-plates containing PDA (potato dextrose agar) media.

The paper disc method, based on diffusion capacity of test chemical(s) through an agar medium, was used for screening the fungicidal potential of metal ferrocyanides against test fungi. Fungal plugs were placed at the centre of assay plate containing sterilized PDA and allowed to grow. After a circular growth of about 2–3 cm diameter, four sterilized paper discs (two loaded with 20 μL of aqueous suspension of metal ferrocyanide and two with same amount of pure solvent) were placed at equal distance from the centre to determine the effect of plant extract on the growth of fungal pathogen. Plates were incubated at 20°C for *M. Perniciosa* and 28°C for *R. solani* and the inhibition zones were measured after one and four days of incubation respectively. Dumbbell-shaped growth was observed in case of complexes possessing the fungicidal activity. The food poisoning technique was used for finding out the per cent inhibition. For this purpose, 20 mg metal ferrocyanide was mixed with 20 mL PDA before pouring into each sterilized petri-dish. The fungal plug was placed at the centre of petri-dish and the petri-plates were placed at the temperatures mentioned above in case of the fungal pathogens involved. Growth of fungus was recorded after two and six days for *R. solani* and *M. perniciosa* respectively. The per cent inhibition was calculated by using the formula of Vincent[11].

$$\text{Inhibition (\%)} = [(C - T)] \times 100$$

where C and T are the growth in mm in control and treatment respectively. All experiments were carried out in triplicate in randomized block design and average values were used for interpretation. The results are presented in Table-1.

TABLE-1
INHIBITORY EFFECT OF TRANSITION METAL FERROCYANIDES AGAINST *M. PERNICIOSA* AND *R. SOLANI*

S. No.	Metal ferrocyanide concentration = 1 mg/mL	*M. perniciosa*		*R. solani*	
		Inhibition zone (mm)	% inhibition	Inhibition zone (mm)	% inhibition
1.	$Mn_2[Fe(CN)_6]\cdot 3H_2O$	2	30	2	20
2.	$Co_2[Fe(CN)_6]\cdot 2H_2O$	0	00	0	00
3.	$Ni_2[(CN)_6]\cdot 5H_2O$	4	60	5	60
4.	$Cu_2[Fe(CN)_6]\cdot 7H_2O$	3	50	3	40
5.	$Zn_2[Fe(CN)_6]\cdot 3H_2O$	2	30	6	90
6.	$Cd_2[Fe(CN)_6]$	0	00	12	100

The values of correlation coefficient (r) and coefficient of determination (r^2) are 0.997 and 0.994 respectively for observations related to the inhibitory effect against *M. perniciosa*. The value of r^2 suggests that 99.4% inhibition was caused by metal ferrocyanides and rest 0.6% may be attributed to other unknown factors. The calculations related to the significance test ('t' test) revealed that the value of 't' (25.73) is much higher than the critical value noted from 't' distribution table for degree of freedom 4 at 5% significance level. This suggests that there are less than 5% chances of error in drawing the conclusions. Further, the calculated value of 'r', 'r^2' and 't' (at 5% significance level), for the observations made in case of *R. solani* are 0.966, 0.933 and (28.84) respectively. These values indicate that a 93.3% inhibition is caused by metal ferrocyanides and rest 6.7% due to other causes. In addition to it, the value of 't' is much higher than the critical value which is indicative of less than 5% chances of occurrence of error, and that the null hypothesis may be safely rejected at 5% significance level.

A perusal of the data (Table-1), reveals that Cd(II) ferrocyanide is not effective against *M. perniciosa* but it is 100% inhibitory to *R. solani*. Further, Co(II) ferrocyanide is not potent against any of the fungal pathogens used. Other metal ferrocyanides are significantly potent against both of the pathogens causing 20–100% inhibition. The results suggest that these complexes may be used as fungicides alone or in combination with other fungicidal substances resulting in the development of ecofriendly fungicides for future that can help in safeguarding our environment.

REFERENCES

1. J. Krtil, *J. Inorg. Nucl. Chem.*, **27**, 233 (1965).
2. W.E. Prout, E.R. Russel and H.J. Groh, *J. Inorg. Nucl. Chem.*, **27**, 473 (1965).
3. L.H. Baetsle, D.V. Deyck and D. Huys, *J. Inorg. Nucl. Chem.*, **27**, 683 (1965).
4. Dutch patent number 282.279 (Aug. 20, 1962) and Belgian patent number PV 509.936 (Aug. 20, 1963).
5. H. Qureshi, K.G. Varshney and F. Khan, *J. Chromatography*, **65**, 547 (1972).
6. Kamaluddin, M. Nath, S.W. Deopujari and A. Sharma, *Origins Life Evol. Biosphere*, **24**, 469 (1994).
7. Kamaluddin, M. Nath and A. Sharma, *Origins Life Evol. Biosphere*, **24**, 469 (1994).
8. S. Viladkar, R. Agarwal and Kamaluddin, *Bull. Chem. Soc. (Japan)*, **69**, 95 (1996).
9. B.E. Bowler, K.J. Ahmad, W.I. Sundgust, L.S. Hollis, E.E. Whang and S.J. Lippard, *J. Am. Chem. Soc.*, **111**, 1299 (1989).
10. V. Kourim, J. Rais and B. Millon, *J. Inorg. Nucl. Chem.*, **26**, 1111 (1964).
11. J.M. Vincent, *Nature*, **159**, 850 (1947).
12. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, New York, p. 166 (1963).

(*Received*: 8 January 2003; *Accepted*: 12 May 2003) AJC-3115